ON VARIATIONAL SOLUTION OF THE FOUR-BODY SANTILLI-SHILLADY MODEL OF H_2 MOLECULE

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Abstract

In this paper, we apply Ritz variational approach to a new isochemical model of H_2 molecule suggested by Santilli and Shillady. We studied Gaussian, V_g, and exponential, V_e, screened Coloumb potential *approximations*, as well as the original Hulten potential, V_h, case. Both the Coloumb and exchange integrals have been calculated only for V_e owing to Gegenbauer expansion while for V_g and V_h cases we achieved analytical results only for the Coloumb integrals. We conclude that the V_e-based model is capable to fit experimental data on H_2 molecule in confirmation of the results of numerical HFR approach by Santilli and Shillady. Also, we achieved the energy-based estimation of the weight of the isoelectronium phase which is appeared to be of the order of 1%...6%, for the case of V_e. However, we note that this is *not* the result corresponding to the original Santilli-Shillady model, which is based on the Hulten potential V_h. An interesting result is that in order to prevent divergency of the Coloumb integral for V_h the correlation length parameter r_c should run discrete set of values. We used this condition in our V_e-based model.

1 Introduction

In this paper, we consider the four-body Santilli-Shillady isochemical model of H_2 molecule [1, 2, 3] characterized by additional short-range attractive Hulten potential between the electrons. This potential is assumed to lead to bound state of electrons called isoelectronium. The restricted three-body Santilli-Shillady model (stable and point-like isoelectronium) of H_2 has been studied in ref. [4], in terms of exact solution. For the mass of isoelectronium $M = 2m_e$, this solution implied much lower energy than the experimental one so we varied the mass and obtained that $M = 0.308381m_e$ fits the experimental binding energy, $E_{exper}[H_2] = -1.174474$ a.u. up to six decimal places, although at bigger value of the internuclear distance, $R = 1.675828$ a.u. in contrast to $R_{exper}[H_2] = 1.4011$ a.u. We realize that the three-body model is capable to represent the binding energy but it is only some approximation to the four-body model, and one should study the general four-body hamiltonian of the Santilli-Shillady model as well.

In the present paper, we use Ritz variational approach to the four-body Santilli-Shillady isochemical model of H_2 molecule, i.e. without restriction that the isoelectronium is stable and point-like particle, in order to find the ground state energy and bond length of the H_2 molecule.

In Sec. 2, we analyze some features of the four-body Santilli-Shillady isochemical model of H_2 molecule.

In Sec. 3, we apply Ritz variational approach to the four-body Santilli-Shillady model of H_2 molecule. We calculate Coloumb integral for the cases of Hulten potential (Sec. 3.1.1), exponential screened Coloumb potential (Sec. 3.1.2), and Gaussian screened Coloumb potential (Sec. 3.1.3). Owing to Gegenbauer expansion, exchange integral has been calculated for the case of exponential screened potential, with some approximation made (Sec. 3.1.4). Exchange integrals for the Hulten potential and the Gaussian screened Coloumb potential have not been derived, and require more study. We present main details of calculations of the Coloumb and exchange integrals which have been appeared to be rather cumbersome, especially in the case of Hulten potential.

In Sec. 3.2, we make numerical fitting of the variational energy for the case of exponential screened Coloumb potential V_e. Also, we estimate the weight of the isoelectronium phase. However, we use all the important results of the analysis made for the Hulten potential V_h.

1) We conclude that the V_e-based model with the one-level isoelectronium is *capable to fit the experimental data on H_2 molecule* (both the binding energy E and the bond length R). This is in confirmation of the results of numerical HFR approach (SASLOBE routine) to the V_g-based model of ref. [1].

2) One of the interesting implications of the Ritz variational approach to the Hulten potential case is that the correlation length parameter r_c, entering the Hulten potential, and, as a consequence, the variational energy, should run discrete set of values during the variation. In other words, this means that *only some fixed values of the effective radius of the one-level isoelectronium are admitted*, in the original Santilli-Shillady model, within the framework of the Ritz approach. This highly remarkable property is specific to the Hulten potential V_h while it is absent in the V_e, or V_g-based models.

3) Also, we achieved an estimation of the *weight of the isoelectronium phase* for the case of V_e-based model which is appeared to be of the order of 1%...6%. This weight has been estimated from the *energy* contribution, related to the exponential screened potential V_e, in comparison to the contribution related to the Coloumb potential.

4) Another general conclusion is that the effective radius of the isoelectronium r_c should be less that 0.25 a.u.

We note that the weight of the phase does not mean directly a time share between the two regimes, i.e., 1...6% of time for the pure isoelectronium regime, and 99...94% of time for the decoupled electrons regime. This means instead *relative contribution to the total energy* provided by the potential V_e and by the usual Coloumb potential between the electrons, respectively. As a consequence, the weight of the isoelectronium phase, which can be thought of as a measure of stability of the isoelectronium, may be

1. Different from the obtained 1...6% when calculated for some other characteristics of the molecule, e.g., for a relative contribution of the pure isoelectronium to the total magnetic moment of the H_2 molecule;

2. Different from the obtained 1...6% for the case of the original Hulten potential V_h.

So, the result of the calculation made in this paper is not the final result implied by the general four-body Santilli-Shillady model of H_2 molecule since the latter model is based on the Hulten potential V_h. This paper can be viewed only as a preliminary study to it. However, we have made some

essential advance in analyzing the original Hulten potential case (Sec. 3.1.1), which we have used in the V_e-based model.

Below, we describe the procedure used in Sec. 3 in a more detail. In Ritz variational approach, the main problem is to calculate analytically so called molecular integrals. The variational molecular energy, in which we are interested in, is expressed in terms of these integrals; see Eq.(3.2). These integrals arise when using some wave function basis (usually it is a simple hydrogen ground state wave functions) in the Schrödinger equation for the molecule. The main idea of the Ritz approach is to introduce parameters into the wave function, and vary them, together with the internuclear distance parameter R, to achieve a minimum of the molecular energy. In the case under study, we have two parameters, γ and ρ, where γ enters hydrogen-like ground state wave function (3.10), and $\rho = \gamma R$ measures internuclear distance. These parameters should be varied (analytically or numerically) in the final analytical expression of the molecular energy, after the calculation is made for the associated molecular integrals.

However, the four-body Santilli-Shillady model of H_2 molecule suggests additional, Hulten potential interaction between the electrons. The Hulten potential contains two parameters, V_0 and r_c, where V_0 is a general factor, and r_c is a correlation length parameter which can be viewed as an effective radius of the isoelectronium; see Eq. (3.23). Thus, we have four parameters to be varied, γ, ρ, V_0, and r_c. The introducing of Hulten potential leads to modification of some molecular integrals, namely, of the Coloumb and exchange integrals; see Eqs. (3.5) and (3.7). The other molecular integrals remain the same as in the case of usual model of H_2, and we use the known analytical results for them. So, we should calculate the associated Coloumb and exchange integrals for the Hulten potential to get the variational energy analytically. In fact, calculating of these integrals, which are six-fold ones, constitutes the main problem here. Normally, Coloumb integral, which can be performed in bispherical coordinates, is much easier than the exchange one, which is performed in bishperoidal coordinates.

Calculation of the Coloumb integral for Hulten potential, V_h, appeared to be rather nontrivial (Sec. 3.1.1). Namely, we used bispherical coordinates, and have faced several special functions, such as polylogarithmic function, Riemann ζ-function, digamma function, and Lerch function, during the calculation. Despite the fact that we see no essential obstacles to calculate this six-fold integral, we stopped the calculation after fifth step because sixth (the

last) step assumes necessity to calculate it separately for each integer value of $\lambda^{-1} \equiv (2\gamma r_c)^{-1}$, together with the need to handle very big number of terms. During the calculations, we were forced to use the condition that λ^{-1} should take integer values in order to prevent divergency of the Coloumb integral for Hulten potential. Namely, some combination of terms containing Lerch functions gives a finite value only if this condition holds. This condition is specific to Hulten potential. Note also that we can not get general form of a final expression for the Coloumb integral for Hulten potential because Lerch functions entering the intermediate expression (after the fifth step, see Eq.(3.80)) can be integrated over only for a concrete numerical value of their third argument.

In order to proceed with the Santilli-Shillady approach, we invoke to two different simplified potentials, the exponential screened Coloumb potential, V_e, and the Gaussian screened Coloumb potential, V_g, instead of the Hulten potential V_h. They both mimic well Hulten potential at short and long range asymptotics, and each contains two parameters, for which we use the notation, A and r_c. In order to reproduce the short range asymptotics of Hulten potential the parameter A should have the value $A = V_0 r_c$, for both the potentials. The Coloumb integrals for these two potentials have been calculated *exactly* (Secs. 3.1.2 and 3.1.3) owing to the fact that they are much simpler than the Hulten potential. Particularly, we note that the final expression of the Coloumb integral for V_g contains only one special function, the error function $\mathrm{erf}(z)$, while for V_e it contains no special functions at all.

Having these results we turned next to the most hard part of work: the exchange integral. Usually, to calculate it one has to use bispheroidal coordinates, and needs in an expansion of the potential in some orthogonal polynomials, such as Legendre polynomials, in bispheroidal coordinates. Here, only the exponential screened potential V_e is known to have such an expansion but it is formulated, however, in terms of bispherical coordinates (the Gegenbauer expansion). Accordingly, we calculated exactly the exchange integral for V_e, at *zero* internuclear separation, $R = 0$, at which case one can use bispherical coordinates. After that, we recovered partially the R dependence using the standard result for the exchange integral for Coloumb potential (Sugiura's result). Thus, we achieved some approximate expression of the exchange integral for the case of V_e. So, all the subsequent results correspond to the V_e-based model.

Inserting obtained V_e-based Coloumb and exchange integrals into the to-

tal molecular energy expression, we get the final analytical expression containing four parameters, γ, ρ, A, and r_c. Prior to going into details of the energy minimization for the V_e-based (approximate) model, we analyze the set of parameters, and the conditions which we derived in the original Hulten potential case.

(1) From the analysis of Hulten potential, we see (Sec. 2.1) that the existence of a bound state of two electrons (which is proper isoelectronium) leads to the following relationship between the parameters for the case of *one* energy level of the electron-electron system: $V_0 = \hbar^2/(2mr_c^2)$. So, using the above mentioned relation $A = V_0 r_c$ we have $A = 1/r_c \equiv 2\gamma/\lambda$, in atomic units ($\hbar = m_e = c = 1$). Thus note that, in this paper, we confined our consideration to the case of *one-level* isoelectronium.

(2) From the analysis of the Coloumb integral for Hulten potential, we see (Sec. 3.1.1) that the condition, $\lambda^{-1} =$ *integer number*, should hold, and one can use it as well.

We use the above two conditions, coming from the Hulten potential analysis, in the energy minimization calculations for the case of our V_e-based model. The first condition diminishes the number of independent parameters by one (they become three, γ, ρ, and λ) while the second condition means a discretization of the λ parameter, $\lambda^{-1} = 4, 5, 6, \ldots$ Here, we used the condition $\lambda^{-1} > 3$ which we obtained during the calculation of the Coloumb integral for V_e.

With the above set up, we minimized the total molecular energy of the V_e-based model. Numerical analysis shows that the λ dependence does not reveal any minimum, in the interval of interest, $4 < \lambda^{-1} < 60$, while we have a minimum of the energy at some values of γ and ρ. So, we calculated the energy minima for different values of λ, in the interval of interest, $4 < \lambda^{-1} < 60$. Results are presented in Tables 2 and 3. One can see that the binding energy decreases with the increase of the parameter r_c, which corresponds to the effective radius of the isoelectronium.

The following remarks are in order.

(i) Note that the discrete character of r_c does not mean that the isoelectronium is some kind of a multilevel system, with different effective radia of isoelectronium assigned to the levels. We remind that we treat the isoelectronium as *one-level* system due to the above mentioned relation $V_0 = \hbar^2/(2mr_c^2)$. In fact, this means that there is a set of one-level isoelectronia of different fixed effective radia from which we should select only one,

to fit the experimental data.

(ii) The use of the exponential screened potential V_e can only be treated as some *approximation* to the original Hulten potential, and, thus, to the original Santilli-Shillady model of H_2 molecule. So, the numerical results obtained in Sec. 3.2 are valid only within this approximation. Hulten potential makes a difference (one can see this, e.g., by comparing Sec. 3.1.1 and Sec. 3.1.2), and it is worth to be investigated more closely by, for example, combination of analytical and numerical methods.

(iii) The results obtained in ref. [1] are based on the Gaussian screened Coloumb potential V_g approximation, to which the present work gives support in the form of exact analytical calculation of the Coloumb integral for V_g (Sec. 3.1.3). Also, the present work gives possibility to make a comparative analysis of ref. [1], due to some similarity of the used potentials, V_e and V_g.

(iv) Both the Coloumb integrals, for V_e and V_g, reveal a minimum in respect with $\lambda = 2\gamma r_c$, i.e. in respect with r_c (see Figures 6 and 9) since minimization in Ritz parameter γ is made independently. In principle, this gives us an opportunity to minimize the total molecular energy E_{mol} with respect to r_c. However, there are two reasons that we can not provide this minimization. First, these minima correspond to rather large values of r_c, namely, $r_c \geq 1$ a.u. for V_e (Fig. 6), and $r_c > 2$ a.u. for V_g (Fig. 9). Of course, this is not an obstacle to do minimization but we note that we generally assume that the effective radius of the isoelectronium r_c is much less than the internuclear distance, $r_c \ll R = R_{exper}[H_2] = 1.4011$ a.u. Second, and the main, reason is that for the exponential screened potential case (Sec. 3.1.2) the parameter λ should be less than 1/3 to provide convergency of the associated Coloumb integral. Typically, $\gamma \simeq 1.2$, from which we obtain the condition $r_c = \lambda/2\gamma < 0.2$ a.u. Also, for the Hulten potential case (Sec. 3.1.1), we obtained $\lambda < 1/2$, and hence $r_c < 0.25$ a.u. This means that, in fact, it is *impossible* to reach finite minimum of the total molecular energy E_{mol} in respect with r_c since the Coloumb integrals blow up, at $r_c > 0.25$ a.u., leading thus to infinite total energy E_{mol}. So, in our approach we arrive at a strict theoretical conclusion that the effective radius of the isoelectronium r_c must be less than 0.25 a.u. Clearly, this supports our assumption that r_c is much less than the internuclear distance R.

2 Santilli-Shillady model and the barrier

In this Section, we consider the general four-body Santilli-Shillady model [1] of H_2 molecule, in Born-Oppenheimer approximation (i.e. at fixed nuclei). Shrödinger equation for H_2 molecule with the additional short range attractive Hulten potential between the electrons is of the following form:

$$\left(-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 - V_0\frac{e^{-r_{12}/r_c}}{1-e^{-r_{12}/r_c}} + \frac{e^2}{r_{12}}\right.$$
$$\left. -\frac{e^2}{r_{1a}} - \frac{e^2}{r_{2a}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2b}} + \frac{e^2}{R}\right)|\psi\rangle = E|\psi\rangle, \tag{2.1}$$

where R is distance between the nuclei a and b.

Interaction between the two electrons in the model is due to the potential

$$V(r_{12}) = V_C(r_{12}) + V_h(r_{12}) = \frac{e^2}{r_{12}} - V_0\frac{e^{-r_{12}/r_c}}{1-e^{-r_{12}/r_c}}, \tag{2.2}$$

where r_{12} is distance between the electrons, V_0 and r_c are real positive parameters. Here, first term, V_C, is usual repulsive Coloumb potential, and the second term, V_h, is an attractive Hulten potential.

Extrema of $V(r_{12})$ are defined by the equation

$$V'(r_{12}) = -\frac{e^2}{r_{12}^2} + \frac{V_0}{r_c}\frac{e^{r_{12}/r_c}}{(e^{r_{12}/r_c}-1)^2} = 0. \tag{2.3}$$

In the limit $r_{12}\to\infty$, potential $V(r_{12}) \sim e^2/r_{12} = V_C(r_{12})$. Series expansion of $V(r_{12})$ at $r_{12}\to 0$ is

$$V(r_{12})|_{r_{12}\to 0} = \frac{e^2 - V_0 r_c}{r_{12}} + \frac{V_0}{2} - \frac{V_0}{12r_c}r_{12} + O(r_{12}^3). \tag{2.4}$$

In general, there is relationship of Hulten potential to Bernoulli polynomials $B_n(x)$. Namely, Bernoulli polynomials are defined due to

$$\frac{se^{xs}}{e^s-1} = \sum_{n=0}^{\infty} B_n(x)\frac{s^n}{n!}, \tag{2.5}$$

and we can reproduce Hulten potential,

$$\frac{e^s}{1-e^s} = -\frac{1}{s}\sum_{n=0}^{\infty} B_n(1)\frac{s^n}{n!}, \tag{2.6}$$

taking $s = -r_{12}/r_c$. First five Bernoulli coefficients are

$$B_0(1) = 1,\ B_1(1) = \frac{1}{2},\ B_2(1) = \frac{1}{6},\ B_3(1) = 0,\ B_4(1) = -\frac{1}{30}. \tag{2.7}$$

Eq.(2.6) means expansion of Hulten potential with the use of Bernoulli coefficients.

Eq.(2.4) implies that to have an *attraction* near $r_{12} = 0$, which is necessary for forming of isoelectronium, we should put the condition

$$V_0 r_c > e^2. \tag{2.8}$$

We note that, in view of the asymptotics (2.4), $Q = \sqrt{V_0 r_c}$ can be thought of as *Hulten charge* of the electrons.

Under this condition, $V(r_{12})$ has one maximum at the point defined by Eq.(2.3). This is the equilibrium point at which the Coloumb potential is equal to the Hulten potential. So, we have barrier (B) separating two asymptotic regions, (A) $r \to 0$ and (C) $r \to \infty$, with Coloumb-like attraction and Coloumb-like repulsion, respectively.

In the region A, attractive Hulten potential V_h dominates, and therefore two electrons form bound state (isoelectronium), while in the region C Coloumb repulsion V_C dominates, and they are separated. This separation is limited by the size of the neutral molecule. For example, assuming that H_2 molecule is in the ground state we have $r \leq r_{mol} = 3.46$ bohrs, where we have assumed that separation between the protons is $R = 1.46$ bohrs $= 0.77 r_{12} A$.

Existence of the bound state of the electrons and of the barrier B is a novel feature provided by the model. The asymptotic states, in regions A and C, pertube each other due to the barrier effect in region B.

2.1 Region A

In the case

$$V_0 r_c \gg e^2 \tag{2.9}$$

we can ignore Coloumb repulsion V_C, and region A is a Hulten region, $|V_h| \gg |V_C|$; see Eq.(2.4). Then, exact solution of one-particle Schrödinger equation with Hulten potential V_h, where wave function has the boundary conditions $\psi(0) = 0$ and $\psi(\infty) = 0$ (see [5], problem 68), can be used to establish the relation between the parameters V_0 and r_c, and to estimate r_c.

Energy spectrum for Hulten potential is given by

$$E_n = -V_0 \left(\frac{\beta^2 - n^2}{2n\beta}\right)^2, \quad n = 1, 2, \ldots. \tag{2.10}$$

where

$$\beta^2 = \frac{2mV_0}{\hbar^2} r_c^2, \tag{2.11}$$

and m is mass of the particle. Assuming that there is only *one* energy level, namely, ground state $n = 1$, we obtain the condition

$$\beta^2 = 1, \tag{2.12}$$

which can be rewritten as

$$r_c = \hbar\sqrt{\frac{1}{2mV_0}}. \tag{2.13}$$

Note that this state is characterized by approximately *zero* energy, $E_1 = 0$, due to Eq.(2.10); strictly speaking, β^2 must be bigger but close to 1 in Eq.(2.12).

We should to note that the number of energy levels for Hulten potential is always finite due to Eq.(2.10). Assumption that there are more than one energy levels in the bound state of two electrons, i.e. that $\beta > 1$, leads to drastical decrease of ground level energy $E_1 < 0$, and relatively small increase of characteristic size of isoelectronium in the ground state.

As the conclusion, the model implies "quantization" of the distance between two electrons, $r = r_{12}$, namely, forming of relatively small quasiparticle (isoelectronium) characterized by total mass $M = 2m_e$, charge $q = -2e$, spin zero, $s = 0$, and small size in the ground one-level state. This quasiparticle, as a strongly correlated system of two electrons, moves in the potential of two protons of H_2 molecule, and one can apply methods developed for H_2^+ ion, with electron replaced by isoelectronium, to calculate approximate energy spectrum of H_2 [4]. However, this quasiparticle is not stable, being a quasi-stationary state, due to finite height and width of the barrier B. So, we must take into account effects of both regions B and C to obtain correct energy spectrum of H_2 molecule, within the framework of the model.

2.2 Region B

Quasiclassically, due to smooth shape of the barrier, and because of exponential decrease of wave functions inside the barrier, electrons are not much time in region B, so we can ignore this *transient phase* in subsequent consideration.

We should to point out that the existence of the bound state in the region A and repulsion in the region C unavoidably leads to existence of the barrier.

2.3 Region C

In general, region C is infinite, $r_C < r < \infty$, where r_C is the distance between two electrons at which the Hulten potential is much smaller than the Coloumb potential, $|V_h| \ll |V_C|$.

In this region, electrons are not strongly correlated, in comparison to that in region A. Here, correlation is due to usual overlapping, Coloumb repulsion, exchange effects, and Coloumb attraction to protons. Shortly, we have the usual set up as it for the standard model of H_2 molecule.

Discarding, for a moment, effects coming from the consideration of regions A and B, we have finite motion of the electrons in region C. Namely, in the ground state of H_2, the distance between electrons is confined by $r = r_{mol} =$ 3.46 bohrs. We restrict consideration by the ground state of H_2 molecule.

Due to this finiteness of the region C, $r < r_{mol}$, two electrons on the same orbit have constant probability to penetrate the barrier to form strongly correlated system, isoelectronium, and vice verca.

2.4 Model of decay of isoelectronium

Below, we assume that the isoelectronium undergoes decay, and the resulting two electrons are separated by sufficiently large distance, in the final state. This leads us to consideration of the *effective life-time of isoelectronium*. To estimate the order of the life-time, we use ordinary formula for radioactive α-decay since the potential $V(r)$ is of the same shape, with very sharp decrease at $r < r_{max}$ and Coloumb repulsion at $r > r_{max}$. This quisiclassical model is a crude approximation because in fact the electrons do not leave the molecule. Moreover, we have the two asymptotic regimes simultaneously, with some distribution of probability, and it would be more justified here to say on

frequency of the decay-formation process. However, due to our assumption of small size of isoelectronium, in comparison to the molecule size, we can study an elementary process of decay separately, and use the notion of life-time.

Decay constant is

$$\lambda = \frac{\hbar D_0}{2mr_{max}^2} \exp\left\{ -\frac{4\pi Z e^2}{\hbar}\sqrt{\frac{m}{2E}} + \frac{4e}{\hbar}\sqrt{Zmr_{max}} \right\}, \tag{2.14}$$

where we put, in atomic units,

$$\hbar = 1,\ e = 1,\ m = 1/2,\ Z = 1,\ r_{max} = 0.048,\ E = 1. \tag{2.15}$$

Here, $E = 1$ a.u. $= 27.212$ eV is double kinetic energy of the electron on first Bohr's orbit, $a_0 = 0.529 r_{12} A$, that corresponds approximately to maximal relative kinetic energy of two electrons in ground state of H_2, and $m = 1/2$ is reduced mass of two electrons.

We obtain the following numerical estimation for the life-time of isoelectronium:

$$1/\lambda = D_0 \cdot 1.6 \cdot 10^{-17}\,\mathrm{sec}, \tag{2.16}$$

i.e. it is of the order of 1 atomic unit of time, $\tau = 2.42 \cdot 10^{-17}$ sec. For lower values of the relative energy E, we obtain longer lifetimes; see Table 2.

The quasiclassical model for decay we are using here is the following. Particle of reduced mass $m = 1/2$ penetrate the barrier B. This means a decay of isoelectronium. In the center of mass of electrons system, electrons undergo Coloumb repulsion and move in opposite directions receiving equal speed so that at large distances, $r \gg r_{max}$, each of them have some kinetic energy. This energy can be given approximate upper estimation using linear velocity of electron on first Bohr's orbit, $v = 2.19 \cdot 10^6$ cm/sec, since electrons are in the ground level of H_2 molecule (this is the effect of the nuclei). This upper estimation corresponds to assumption of zero velocity of the center of mass in respect to protons which we adopt here. Kinetic energy of the particle of reduced mass is then double kinetic energy of electron, in center of mass system.

As the conclusion, in the framework of the model, H_2 molecule can be viewed as a mixed state of H_2^+ ion like system, i.e. *strongly correlated phase* (Hulten phase), when electrons form isoelectronium, and standard model of

Energy E, a.u.	eV	Lifetime, D_0·sec
2	54.4	$2.6 \cdot 10^{-18}$
1	27.2	$1.6 \cdot 10^{-17}$
0.5	13.6	$2.2 \cdot 10^{-16}$
0.037	1	$5.1 \cdot 10^{-6}$
0.018	0.5	4.0
0.0018	0.1	$3.1 \cdot 10^{+25}$

Table 1: Lifetime of isoelectronium. E is relative kinetic energy of the electrons, at large distances, $r \gg r_{max}$, in the center of mass system.

H_2, i.e. *weakly correlated phase* (Coloumb phase), when electrons are separated by large distance, $r > r_{max}$. Note that, as it has been mentioned above, we ignore the *transient phase* (inside the barrier) in this consideration. Evidently, the (statistical) weight of each phase depends on the characteristics of the potential $V(r_{12})$.

For extremally high barrier, only one of the phases could be realized with some energy spectra in each phase, namely, either spectrum of H_2^+ ion like system (with electron replaced by isoelectronium), or usual spectrum of H_2 molecule (without Hulten potential), respectively.

For high but finite barrier, each phase receives perturbation, and their (ground) energy levels split to two levels corresponding to *simultaneous* realization of both the phases. Note that the value V_{max} is indeed high, $V_{max} \sim 500$ eV, under the given values of the parameters.

In general, existence of the strongly correlated phase (isoelectronium) leads to *increase* of the predicted dissociation energy, D, of H_2 molecule. Indeed, the mutual infuence of the regions A and C decreases the ground energy level E of H_2 due to the above mentioned splitting. The general formula for D is

$$D = 2E_0 - (E + \frac{1}{2}\hbar\omega), \tag{2.17}$$

where $2E_0 = -1$ is total energy of two separated H atoms, and $\frac{1}{2}\hbar\omega$ is zero mode energy of the protons in H_2. So, decreasing of $E < 0$ causes increase of D.

It is remarkable to note that experimental data give dissociation energy

$D_{exper}[H_2] = 4.45$ eV for H_2 molecule (see, e.g. [5] and references therein) while theoretical predictions within the standard model are $D = 2.90$ eV (Heitler-London), $D = 3.75$ eV (Flugge), and $D = 4.37$ eV (Hylleraas). We observe that improvement of the variational approximation gives better fits but still it gives *lower* values (about 2% lower) partially due to the fact that variational technique used there predicts generally bigger value (upper limit) for the ground energy.

Below, we use the same Ritz variational technique as it had been used by Heitler, London and Hylleraas but the feature of the model is the existence of additional attractive short range potential between the electrons suggested by Santilli and Shillady.

3 Variational solution for ground state energy of H_2 molecule

In the limiting case of large distances between the nuclei, $R \to \infty$, we have the total wave function of the electrons in the form

$$|\psi\rangle = f(r_{a1})f(r_{b2}) \pm f(r_{b1})f(r_{a2}), \tag{3.1}$$

where the first term corresponds to the case when electron 1 is placed close to nucleus a and $f(r_{a1})$ is wave function of the corresponding separate H atom while the second term corresponds to the case when electron 1 is placed close to nucleus b. Symmetrized combination ($'+'$ sign) corresponds to antiparallel spins of the electrons 1 and 2, and, as the result of the usual analysis, leads to attraction between the H atoms. Below, we use this symmetrized representation of the total wave function as the approximation to exact wave function.

3.1 Analytical calculations

By using Ritz variational approach and representation (3.1), we obtain from the Schrödinger equation (2.1) the energy of H_2 molecule in the following form (cf. [5]),

$$E_{mol} = 2\frac{\mathcal{A} + \mathcal{A}'\mathcal{S}}{1 + \mathcal{S}^2} - \frac{2(\mathcal{C} + \mathcal{E}\mathcal{S}) - (\mathcal{C}' + \mathcal{E}')}{1 + \mathcal{S}^2} + \frac{1}{R}, \tag{3.2}$$

where

$$\mathcal{S} = \int dv \; f^*(r_{a1}) f(r_{b1}) \tag{3.3}$$

is overlap integral,

$$\mathcal{C} = \int dv \; \frac{1}{r_{b1}} |f(r_{a1})|^2, \tag{3.4}$$

$$\mathcal{C}' = \int dv_1 dv_2 \; \left(\frac{1}{r_{12}} - V_0 \frac{e^{-r_{12}/r_c}}{1 - e^{-r_{12}/r_c}} \right) |f(r_{a1})|^2 |f(r_{b2})|^2, \tag{3.5}$$

are Coloumb integrals,

$$\mathcal{E} = \int dv \; \frac{1}{r_{a1}} f^*(r_{a1}) f(r_{b1}), \tag{3.6}$$

$$\mathcal{E}' = \int dv_1 dv_2 \; \left(\frac{1}{r_{12}} - V_0 \frac{e^{-r_{12}/r_c}}{1 - e^{-r_{12}/r_c}} \right) f^*(r_{a1}) f(r_{b1}) f^*(r_{a2}) f(r_{b2}) \tag{3.7}$$

are exchange integrals,

$$\mathcal{A} = \int dv \; f^*(r_{a1}) \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{a1}} \right) f(r_{a1}) \tag{3.8}$$

and

$$\mathcal{A}' = \int dv \; f^*(r_{a1}) \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{b1}} \right) f(r_{b1}). \tag{3.9}$$

We use atomic units, $e = 1$, $m_1 = m_2 = m_e = 1$.

Quite natural choice is that the wave functions in Eq.(3.1) are taken in the form of hydrogen ground state wave function,

$$f(r) = \sqrt{\frac{\gamma^3}{\pi}} e^{-\gamma r}, \tag{3.10}$$

where γ is Ritz variational parameter (γ=1 for the proper hydrogen wave function), and $r = r_{a1}, r_{b1}, r_{a2}, r_{b2}$. With the help of γ we should make better approximation to an exact wave function of the ground state. Namely, we should calculate all the integrals presented above analytically, and then vary the parameters γ away from the value $\gamma = 1$ and R in some appropriate region, say $1 < R < 2$, to minimize the energy (3.2). As the energy minimum will be identified the found value of the parameter R corresponds to

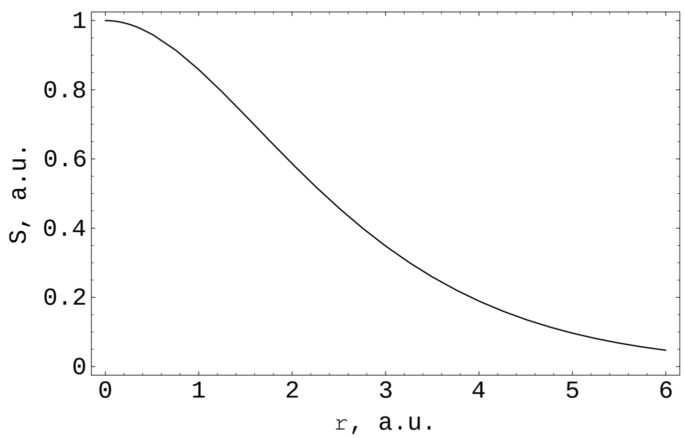

Figure 1: The overlap integral $\mathcal{S}$ as a function of ρ, Eq. (3.11). Here, $\rho = \gamma R$, where γ is Ritz parameter and R is the internuclear distance.

optimal distance between the nuclei. This value should be compared to the experimental value of R.

All the molecular integrals (3.3)-(3.9), except for the Hulten potential parts in (3.5) and (3.7), are wellknown and can be calculated exactly; see, e.g. [5]. Namely, they are

$$\mathcal{S} = \left(1 + \rho + \frac{1}{3}\rho^2\right) e^{-\rho}, \tag{3.11}$$

$$\mathcal{C} \equiv \mathcal{C}_C = \frac{\gamma}{\rho}(1 - (1+\rho)e^{-2\rho}), \tag{3.12}$$

$$\mathcal{C}'_C \equiv \mathcal{C}'_{|V_0=0} = \frac{\gamma}{\rho}\Big(1 - (1 + \frac{11}{8}\rho + \frac{3}{4}\rho^2 + \frac{1}{6}\rho^3)e^{-2\rho}\Big), \tag{3.13}$$

$$\mathcal{E} \equiv \mathcal{E}_C = \gamma(1+\rho)e^{-\rho}, \tag{3.14}$$

$$\mathcal{E}'_C \equiv \mathcal{E}'_{|V_0=0} = \gamma\left(\frac{5}{8} + \frac{23}{20}\rho - \frac{3}{5}\rho^2 - \frac{1}{15}\rho^3\right) e^{-2\rho} + \frac{6\gamma}{5}\frac{h(\rho)}{\rho}, \tag{3.15}$$

$$h(\rho) = \mathcal{S}^2(\rho)(\ln\rho + C) - \mathcal{S}^2(-\rho)E_1(4\rho) + 2\mathcal{S}(\rho)\mathcal{S}(-\rho)E_1(2\rho), \tag{3.16}$$

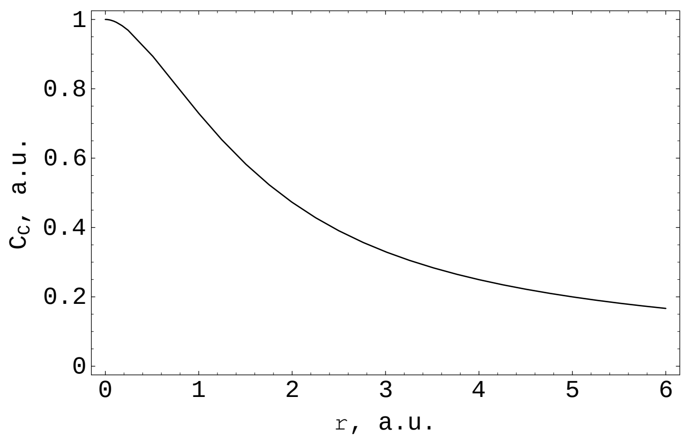

Figure 2: The Coloumb integral $\mathcal{C}_C$ as a function of ρ, Eq. (3.12).

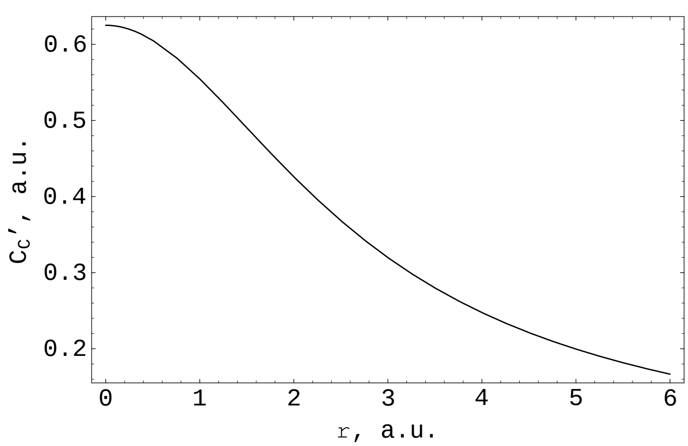

Figure 3: The Coloumb integral $\mathcal{C}_C'$ as a function of ρ, Eq. (3.13).

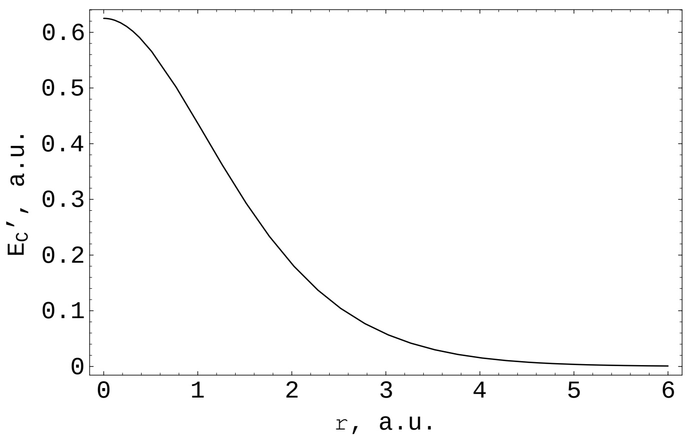

Figure 4: The exchange integral $\mathcal{E}'_C$ as a function of ρ, Eq. (3.15).

$$E_1(\rho) = \int\limits_{\rho}^{\infty} \frac{e^{-t}}{t} dt, \tag{3.17}$$

$$\mathcal{A} = -\frac{1}{2}\gamma^2 + \gamma(\gamma-1), \quad \mathcal{A}' = -\frac{1}{2}\gamma^2\mathcal{S} + \gamma(\gamma-1)\mathcal{E}, \tag{3.18}$$

where C is Euler constant, and we have denoted

$$\rho = \gamma R, \tag{3.19}$$

which can be taken as a second Ritz variational parameter in addition to γ. The most hard part of work here is the exchange integral (3.15), which was calculated for the first time by Sugiura (1927), and contains one special function, the exponential integral function $E_1(\rho)$.

Our problem is thus to calculate analytically the Hulten potential parts of the Coloumb integral (3.5) and of the exchange integral (3.7), and then vary all the Ritz variational parameters in order to minimize the ground state energy (3.2),

$$E_{mol}(\text{parameters}) = \text{minimum}. \tag{3.20}$$

In general, we have four parameters in our problem, $E_{mol} = E_{mol}(\gamma, \rho, V_0, r_c)$, with the first two parameters characterizing inverse radius of electronic orbit

and the internuclear distance, respectively, and the last two parameters coming from the Hulten potential. However, assuming that the isoelectronium is characterized by *one* energy level, i.e. $\beta = 1$, we have the relation (2.13) between V_0 and r_c so that we are left with *three* independent parameters, say, $E_{mol} = E_{mol}(\gamma, \rho, r_c)$. In fact, we have three independent parameters for *any* fixed number β of the levels due to the general relation (2.11),

$$V_0 = \frac{\beta^2 \hbar^2}{2mr_c^2}, \quad \beta = 1, 2, \ldots . \tag{3.21}$$

Behavior of the energy E_{mol} as a function of γ and ρ is more or less clear owing to known variational analysis of the standard model of H_2 molecule. Namely, E_{mol} reveals a local minimum at some values of γ and ρ. Thus, we should closely analyze the r_c dependence of the energy which is specific to the Santilli-Shillady model of H_2 molecule.

Below, we turn to the Coloumb integral for the Hulten potential.

3.1.1 Coloumb integral for Hulten potential

To calculate the Hulten part of the Coloumb integral (3.5) we use spherical coordinates, $(r_{b2}, \theta_2, \varphi_2)$, when integrating over second electron, and $(r_{b1}, \theta_1, \varphi_1)$, when integrating over first electron.

The integral is

$$\mathcal{C}'_h = 4\pi^2 \int\limits_0^\pi d\theta_1 \int\limits_0^\infty dr_{b1} \int\limits_0^\pi d\theta_2 \int\limits_0^\infty dr_{b2}\; V_h(r_{12}) \Big(\frac{\gamma^3}{\pi} e^{-2\gamma r_{b2}} {r_{b2}}^2 \sin\theta_2\Big) \times \tag{3.22}$$

$$\times \Big(\frac{\gamma^3}{\pi} e^{-2\gamma\sqrt{{r_{b1}}^2 + R^2 - {r_{b1}}^2 R\cos\theta_1}} {r_{b1}}^2 \sin\theta_1\Big),$$

where Hulten potential is

$$V_h(r_{12}) = V_0 \frac{e^{-\sqrt{{r_{b2}}^2 + {r_{b1}}^2 - 2r_{b2}r_{b1}\cos\theta_2}/r_c}}{1 - e^{-\sqrt{{r_{b2}}^2 + {r_{b1}}^2 - 2r_{b2}r_{b1}\cos\theta_2}/r_c}}. \tag{3.23}$$

Here, we have used

$$r_{a1} = \sqrt{{r_{b1}}^2 + R^2 - {r_{b1}}^2 R\cos\theta_1},$$

$$r_{12} = \sqrt{{r_{b2}}^2 + {r_{b1}}^2 - 2r_{b2}r_{b1}\cos\theta_2},$$

and the fact that integrals over azimuthal angles φ_1 and φ_2 give us $4\pi^2$.

First, we integrate over coordinates of second electron,

$$I = 2\pi \int_0^{\pi} d\theta_2 \int_0^{\infty} dr_{b2}\ V_h(r_{12})\Big(\frac{\gamma^3}{\pi}e^{-2\gamma r_{b2}}{r_{b2}}^2\sin\theta_2\Big). \tag{3.24}$$

Integration over θ_2 gives us

$$I = \int_0^{\infty} dr_{b2}\ (I_1 + I_2 + I_3 + I_4 + I_5), \tag{3.25}$$

where

$$I_1 = -4\gamma^3 e^{-2\gamma r_{b2}}{r_{b2}}^2, \tag{3.26}$$

$$I_2 = -2\gamma^3 r_c \frac{r_{b2}}{r_{b1}}\sqrt{(r_{b1}-r_{b2})^2}e^{-2\gamma r_{b2}}\ln(1-e^{\sqrt{(r_{b1}-r_{b2})^2}/r_c}), \tag{3.27}$$

$$I_3 = -2\gamma^3 r_c \frac{r_{b2}}{r_{b1}}\sqrt{(r_{b1}+r_{b2})^2}e^{-2\gamma r_{b2}}\ln(1-e^{\sqrt{(r_{b1}+r_{b2})^2}/r_c}), \tag{3.28}$$

$$I_4 = 2\gamma^3 {r_c}^2 \frac{r_{b2}}{r_{b1}}e^{-2\gamma r_{b2}}Li_2(e^{\sqrt{(r_{b1}-r_{b2})^2}/r_c}), \tag{3.29}$$

$$I_5 = 2\gamma^3 {r_c}^2 \frac{r_{b2}}{r_{b1}}e^{-2\gamma r_{b2}}Li_2(e^{\sqrt{(r_{b1}+r_{b2})^2}/r_c}), \tag{3.30}$$

and

$$Li_2(z) = \sum_{k=1}^{\infty}\frac{z^k}{k^2} = \int_z^0 \frac{\ln(1-t)}{t}dt \tag{3.31}$$

is dilogarithm function.

Now, we turn to integrating over r_{b2}. For I_1 we have

$$\int_0^{\infty} dr_{b2}\ I_1 = -1. \tag{3.32}$$

In I_2, we should keep $(r_{b1} - r_{b2})$ to be positive so we write down two separate terms,

$$\int_0^{\infty} dr_{b2} I_2 = I_{21} + I_{22} \equiv \int_0^{r_{b1}} dr_{b2}\ I_2(r_{b2} < r_{b1}) + \int_{r_{b1}}^{\infty} dr_{b2}\ I_2(r_{b2} > r_{b1}). \tag{3.33}$$

In these two integrals, I_{21} and I_{22}, we change variable r_{b2} to x and y, respectively,

$$x = (r_{b1} - r_{b2})/r_c, \quad r_{b1}/r_c < x < 0, \quad y = (r_{b2} - r_{b1})/r_c, \quad 0 < y < \infty, \tag{3.34}$$

in order to simplify integrating. In terms of these variables, we have

$$I_{21} = \int\limits_{r_{b1}/r_c}^{0} dx \; 2\gamma^3 {r_c}^3 (x - \frac{r_c}{r_{b1}} x^2) e^{-2\gamma(r_{b1} - r_c x)} \ln(1 - e^x), \tag{3.35}$$

$$I_{22} = -\int\limits_{0}^{\infty} dy \; 2\gamma^3 {r_c}^3 (y + \frac{r_c}{r_{b1}} y^2) e^{-2\gamma(r_{b1} + r_c y)} \ln(1 - e^y). \tag{3.36}$$

We are unable to perform these integrals directly. To calculate these integrals we use method of differentiating in parameter. Namely, we use simpler integrals,

$$L_1 = \int dx \; e^{2\gamma r_c x} \ln(1 - e^x) \tag{3.37}$$

and

$$L_2 = \int dy \; e^{-2\gamma r_c y} \ln(1 - e^y), \tag{3.38}$$

and differentiate them in parameter r_c to reproduce I_{21} and I_{22}. (One can use parameter γ for this purpose, or introduce an independent parameter putting it to one after making calculations, with the same result.) Namely, by using definitions of L_1 and L_2 we have

$$I_{21} = 2\gamma^3 {r_c}^3 (\frac{1}{2}\frac{d}{dr_c} L_1 - \frac{r_c}{4r_{b1}} \frac{d^2}{d{r_c}^2} L_1) \mid_{x=r_{b1}/r_c}^{x=0}, \tag{3.39}$$

$$I_{22} = -2\gamma^3 {r_c}^3 (-\frac{1}{2}\frac{d}{dr_c} L_2 - \frac{r_c}{4r_{b1}} \frac{d^2}{d{r_c}^2} L_2) \mid_{y=0}^{y=\infty}. \tag{3.40}$$

Now, the problem is to calculate indefinite integrals, L_1 and L_2, which make basis for further algebraic calculations. After making the calculations, we have

$$L_1 = \frac{1}{4\gamma^2 {r_c}^2} e^{2\gamma r_c} \Big(2\gamma r_c (\Phi(e^x, 1, 2\gamma r_c) + \ln(1 - e^x)) - 1 \Big) \tag{3.41}$$

and

$$L_2 = -\frac{1}{4\gamma^2 {r_c}^2} e^{-2\gamma r_c} \Big(2\gamma r_c (\Phi(e^y, 1, -2\gamma r_c) + \ln(1-e^y)) + 1 \Big), \qquad (3.42)$$

where

$$\Phi(z,s,a) = \sum_{k=0}^{\infty} \frac{z^k}{(a+k)^s}, \quad a+k \neq 0, \qquad (3.43)$$

is *Lerch function*, which is a generalization of polylogarithm function $Li_n(z)$ and Riemann ζ-function. Particularly, $Li_2(z) = \Phi(z,2,0)$. Also, we note that the Lerch function arises when dealing with Fermi-Dirac distribution, e.g.,

$$\int_0^{\infty} dk \, \frac{k^s}{e^{k-\mu}+1} = e^{\mu} \Gamma(s+1) \Phi(-e^{\mu}, s+1, 1). \qquad (3.44)$$

Below, we will need in derivatives of Lerch function $\Phi(z,s,a)$ in third argument. By using the definition (3.43) we obtain directly

$$\frac{d}{da} \Phi(z,s,a) \equiv \Phi'(z,s,a) = -s\Phi(z,s+1,a), \qquad (3.45)$$

$$\frac{d^2}{da^2} \Phi(z,s,a) \equiv \Phi''(z,s,a) = s(s+1)\Phi(z,s+2,a). \qquad (3.46)$$

Inserting (3.41) and (3.42) into (3.39) and (3.40) we get

$$I_{21} = \frac{1}{4\gamma r_{b1}} \Big(e^{-2\gamma(r_{b1}-r_c x)} (3 + 2\gamma(r_{b1} - (2+\gamma r_{b1}) r_c x + \gamma {r_c}^2 x^2) - \qquad (3.47)$$

$$-2\gamma r_c ((1 + \gamma(r_{b1} - 2(1+\gamma r_{b1}) r_c x + 2\gamma {r_c}^2 x^2)) [\Phi(e^x, 1, 2\gamma r_c) + \ln(1-e^x)] +$$

$$+2\gamma r_c (-(1 + \gamma(r_{b1} - 2 r_c x)) \Phi'(e^x, 1, 2\gamma r_c) + \gamma r_c \Phi''(e^x, 1, 2\gamma r_c))) \Big) \Big|_{x=r_{b1}/r_c}^{x=0},$$

$$I_{22} = \frac{1}{4\gamma r_{b1}} \Big(e^{-2\gamma(r_{b1}+r_c x)} (3 + 2\gamma(r_{b1} + (2+\gamma r_{b1}) r_c x + \gamma {r_c}^2 x^2) + \qquad (3.48)$$

$$+2\gamma r_c ((1 + \gamma(r_{b1} + 2(1+\gamma r_{b1}) r_c x + 2\gamma {r_c}^2 x^2)) [\Phi(e^x, 1, -2\gamma r_c) + \ln(1-e^x)] +$$

$$+2\gamma r_c ((1 + \gamma(r_{b1} + 2 r_c x)) \Phi'(e^x, 1, -2\gamma r_c) + \gamma r_c \Phi''(e^x, 1, -2\gamma r_c))) \Big) \Big|_{y=0}^{y=\infty}.$$

Now, we have to use the above derivatives (3.45) and (3.46) of Lerch function to obtain final expressions for I_{21} and I_{22}. Then, we should take the limits

$x \to r_{b1}/r_c$, $x \to 0$, and $y \to 0$, $y \to \infty$, respectively. The endpoints $x = r_{b1}/r_c$ and $y = \infty$ can be inserted easily, with the endpoint $y = \infty$ yielding zero, while the limits $x \to 0$ and $y \to 0$ require some care because of the presence of some divergent terms.

To collect all the terms, we sum up I_{21} and $(-1)I_{22}$ given by (3.47) and (3.48), put $x = y$, and take common limit $x \to 0$, inserting $x = 0$ for polynomial and exponential (welldefined) terms. We get

$$I_{21} - I_{22}|_{x\to 0} =$$

$$= -\frac{1}{2r_{b1}}\Big(r_c e^{-2\gamma r_{b1}}(2\gamma r_c(1+\gamma r_{b1})[\Phi(e^x,2,2\gamma r_c) - \Phi(e^x,2,-2\gamma r_c)] + \tag{3.49}$$
$$+4\gamma^2 {r_c}^2[\Phi(e^x,3,2\gamma r_c) + \Phi(e^x,3,-2\gamma r_c)] +$$
$$+(1+\gamma r_{b1})[\Phi(e^x,1,2\gamma r_c) + \Phi(e^x,1,-2\gamma r_c) - 2\ln(1-e^x)]\Big)|_{x\to 0}$$

The limits of Lerch functions of second, $\Phi(e^x, 2, \pm 2\gamma r_c)$, and third, $\Phi(e^x, 3, \pm 2\gamma r_c)$, order, at $x \to 0$, are welldefined while each of the terms in

$$B(2\gamma r_c) \equiv \lim_{x\to 0}[\Phi(e^x,1,2\gamma r_c) + \Phi(e^x,1,-2\gamma r_c) - 2\ln(1-e^x)] \tag{3.50}$$

is *divergent* since Lerch function of first order, $\Phi(e^x, 1, \pm 2\gamma r_c)$, increases unboundedly at $x \to 0$. We will analyze this limit below, to identify the condition at which the divergencies cancel each other. Now, we collect all the terms obtaining final result for the integral in the form

$$\int_0^\infty dr_{b2}\ I_2 = \frac{1}{4r_{b1}}\Big(\frac{1}{\gamma}(-3 + 2\gamma r_{b1} + 8\gamma^3 {r_c}^3\Phi(e^{r_{b1}/r_c},3,2\gamma r_c) + \tag{3.51}$$

$$+2\gamma r_c(1-\gamma r_c)[\Phi(e^{r_{b1}/r_c},1,2\gamma r_c) + 2\gamma r_c\Phi(e^{r_{b1}/r_c},2,2\gamma r_c) + \ln(1-e^{r_{b1}/r_c})]) -$$
$$-2r_c e^{-2\gamma r_{b1}}(1+\gamma r_{b1})\{B(2\gamma r_c) + 2\gamma r_c[\zeta(2,2\gamma r_c) - \zeta(2,-2\gamma r_c)] +$$
$$+4\gamma^2 {r_c}^2[\zeta(3,2\gamma r_c) + \zeta(3,-2\gamma r_c)]\}\Big),$$

where

$$\zeta(s,a) = \sum_{k=1}^{\infty}\frac{1}{(a+k)^s}, \quad a+k \neq 0, \tag{3.52}$$

is generalized Riemann ζ-function. The values of $\zeta(2, \pm 2\gamma r_c)$ and $\zeta(3, \pm 2\gamma r_c)$ entering (3.51) are welldefined. For example, at $\gamma = 1.4$ and $r_c = 0.0048$, we have

$$\zeta(2, \pm 2\gamma r_c) \simeq 5537, \quad \zeta(3, \pm 2\gamma r_c) \simeq 2462. \tag{3.53}$$

Now, we turn to close consideration of the limit (3.50) entering (3.51). Let us calculate it for the particular value $2\gamma r_c = 1/100$. Using expansion of each term of B around $x = 0$, we obtain

$$B(\frac{1}{100}) = \lim_{s\to 1}\Big[100 - \frac{1}{\Gamma(\frac{1}{100})}\{100\Gamma(\frac{101}{100})(C + \ln(1-s) + \psi(\frac{1}{100}))\} - \tag{3.54}$$

$$-\frac{1}{99\Gamma(\frac{99}{100})}\{100\Gamma(\frac{199}{100})(C + \ln(1-s) + \psi(\frac{99}{100}))\} + 2\ln(1-s) + O(1-s)\Big],$$

where we have denoted, for brevity, $s = e^x$,

$$\psi(z) = \sum_{n=0}^{\infty} \frac{1}{z+n} = \frac{\Gamma'(z)}{\Gamma(z)} \tag{3.55}$$

is digamma function, $\Gamma(z)$ is Euler gamma function, and C is Euler constant. Using elementary properties of gamma function we obtain from Eq.(3.54)

$$B(\frac{1}{100}) = 100 - 2C - \psi(\frac{1}{100}) - \psi(\frac{99}{100}), \tag{3.56}$$

so one can see that the logarithmic divergent terms cancel each other, and the limit is welldefined for $2\gamma r_c = 1/100$. The same is true for any *integer* value of

$$k = \frac{1}{2\gamma r_c} \tag{3.57}$$

while at noninteger k the limit $B(\frac{1}{k})$ blows up. Generalizing the above particular result (3.56), we can write down

$$B(\frac{1}{k}) = k - 2C - \psi(\frac{1}{k}) - \psi(1 - \frac{1}{k}), \tag{3.58}$$

for any integer $k > 2$.

This highly remarkable result means that to have finite value of the Coloumb integral we should use the condition that $\lambda^{-1} \equiv (2\gamma r_c)^{-1} = k$

is an integer number. Recalling that typically $\gamma \simeq 1.5$ and $r_c \simeq 0.01$ we have the integer number $k \simeq 30$.

Now, we turn to the next integral, I_3. It is similar to I_2 so that we present the final expression,

$$\int\limits_0^\infty dr_{b2}\, I_3 = \frac{1}{4\gamma r_{b2}}\Big(3+2\gamma r_{b1}+2\gamma r_c(1+\gamma r_{b1})[\Phi(e^{r_{b1}/r_c},1,-2\gamma r_c)+\ln(1-e^{r_{b1}/r_c})]$$
$$-4\gamma^2 {r_c}^2(1+\gamma r_{b1})\Phi(e^{r_{b1}/r_c},2,-2\gamma r_c)+8\gamma^3 {r_c}^3\Phi(e^{r_{b1}/r_c},3,-2\gamma r_c)\Big). \tag{3.59}$$

The integral I_4 is more complicated,

$$\int\limits_0^\infty dr_{b2}\ I_4 = I_{41}+I_{42}, \tag{3.60}$$

where

$$I_{41} = \int\limits_0^{r_{b1}} dr_{b2} 2\gamma^3 {r_c}^2 \frac{r_{b2}}{r_{b1}} e^{-2\gamma r_{b2}} Li_2(e^{(r_{b1}-r_{b2})/r_c}), \tag{3.61}$$

$$I_{42} = \int\limits_{r_{b1}}^{\infty} dr_{b2} 2\gamma^3 {r_c}^2 \frac{r_{b2}}{r_{b1}} e^{-2\gamma r_{b2}} Li_2(e^{(r_{b2}-r_{b1})/r_c}). \tag{3.62}$$

Introducing variables

$$x = (r_{b1}-r_{b2})/r_c, \quad y = (r_{b2}-r_{b1})/r_c, \tag{3.63}$$

we rewrite the integrals in the form

$$I_{41} = \int\limits_{r_{b1}/r_c}^{0} dx\ 2\gamma^3 {r_c}^3 e^{2\gamma(r_{b1}-r_c x)}[Li_2(e^x) - \frac{r_c}{r_{b1}} x Li_2(e^x)], \tag{3.64}$$

$$I_{42} = -\int\limits_0^\infty dy\ 2\gamma^3 {r_c}^3 e^{2\gamma(r_{b1}+r_c y)}[Li_2(e^y) + \frac{r_c}{r_{b1}} y Li_2(e^y)]. \tag{3.65}$$

In the r.h.s. of I_{41}, the first term can be calculated directly in terms of Lerch function while the second term can be obtained from the first term by

differentiating it in the parameter, for which we choose again r_c. Namely, the basic integral, which we will use to calculate I_{41}, is

$$M_1 = \int_{x_0}^{0} dx\ e^{2\gamma r_c x} Li_2(e^x), \tag{3.66}$$

for which we have

$$M_1 = \frac{1}{24\gamma^3 {r_c}^3 \Gamma(2\gamma r_c)} \Big(3(e^{2\gamma r_c x_0} - 1)\Gamma(2\gamma r_c) + \tag{3.67}$$

$$+\Gamma(1+2\gamma r_c)(\gamma r_c \pi^2 - 3C - 3\psi(2\gamma r_c)) -$$

$$-3e^{2\gamma r_c x_0}\Gamma(1+2\gamma r_c)(\Phi(e^{x_0}, 1, 2\gamma r_c) + \ln(1-e^{x_0}) + 2\gamma r_c Li_2(e^{x_0}))\Big).$$

We use this result in the first term of I_{41}. Differentiating M_1 given by Eqs. (3.66) and (3.67) in r_c, we reproduce the second term of I_{41}, up to a factor. So, collecting these results and inserting $x_0 = r_{b1}/r_c$ we obtain after some algebra

$$I_{41} = -\frac{1}{12 r_{b1}\Gamma(1+2\gamma r_c)} \Big(e^{-2\gamma r_c}[r_c(9 + 4\pi^2\gamma^3 {r_c}^2 r_{b1})\Gamma(2\gamma r_c) + \tag{3.68}$$

$$\Gamma(1+2\gamma r_c)(6Cr_c - 3r_{b1} - 6C\gamma r_c r_{b1} - \pi^2 \gamma {r_c}^2 - 6(\gamma r_{b1} - 1) r_c \psi(2\gamma r_c) -$$

$$-6\gamma {r_c}^2 \psi'(2\gamma r_c))] + 3(2r_{b1}\Gamma(1+2\gamma r_c) - 3r_c\Gamma(2\gamma r_c) +$$

$$+2r_c\Gamma(1+2\gamma r_c)[(1-2\gamma r_{b1})\Phi(e^{r_{b1}/r_c}, 1, 2\gamma r_c) + \gamma r_c \Phi(e^{r_{b1}/r_c}, 2, 2\gamma r_c) +$$

$$+(1-2\gamma r_{b1})\ln(1-e^{r_{b1}/r_c}) + \gamma(1-4\gamma r_{b1}) r_c \psi'(e^{r_{b1}/r_c})]\Big),$$

where $\psi'(z) = d\psi(z)/dz$ is derivative of digamma function.

To calculate I_{42} we use a similar method. However, care should be exerted when taking limit $y \to 0$. The basic integral, which we will use to calculate I_{42}, is

$$M_2 = -\int dy\ e^{2\gamma r_c y} Li_2(e^{-y}), \tag{3.69}$$

where we have replaced $y \to -y$ so that the endpoints will be due to $0 < y < -\infty$. The result for M_2 is

$$M_2 = \frac{1}{8\gamma^3 {r_c}^3} e^{2\gamma r_c y}(1 + 2\gamma r_c e^y \Phi(e^y, 1, 1+2\gamma r_c) + 2\gamma r_c \ln(1-e^{-y}) - \tag{3.70}$$

$$-4\gamma^2 {r_c}^2 Li_2(e^{-y})).$$

We should insert here the endpoints $y = 0$ and $y = -\infty$. In the limit $y \to -\infty$, M_2 is zero. In the limit $y \to 0$, we have

$$Li_2(e^{-y})|_{y\to 0} = \frac{\pi^2}{6} \tag{3.71}$$

and, assuming that $k = 1/(2\gamma r_c)$ is an integer number,

$$\Phi(e^y, 1, 1 + 2\gamma r_c) + \ln(1 - e^{-y})|_{y\to 0} = -(\frac{1}{2\gamma r_c} + C + \psi(2\gamma r_c)). \tag{3.72}$$

Thus,

$$M_2|_{y=0}^{y=-\infty} = \frac{1}{12\gamma^2 {r_c}^2}(3C + \pi^2\gamma r_c + 3\psi(2\gamma r_c)), \tag{3.73}$$

for integer k. We should point out that, in the case of noninteger k, M_2 increases unboundedly at $y \to 0$. Using this result in I_{42}, we obtain

$$I_{42} = -\frac{r_c}{12 r_{b1}} e^{-2\gamma r_{b1}} \Big(6C(1 + \gamma r_{b1}) + \pi^2\gamma r_c + 2\pi^2\gamma^2 r_c r_{b1} + \tag{3.74}$$

$$+6(1 + \gamma r_{b1})\psi(2\gamma r_c) - 6\gamma r_c \psi'(2\gamma r_c)\Big).$$

Summing up I_{41} given by (3.68) and I_{42} given by (3.74), we get

$$\int\limits_0^\infty dr_{b2}\ I_4 == \frac{1}{4 r_{b1}\Gamma(1 + 2\gamma r_c)}\Big(3 r_c \Gamma(2\gamma r_c) + e^{-2\gamma r_c}[-r_{b1}\Gamma(1 + 2\gamma r_c) + \tag{3.75}$$

$$+r_c(-3\Gamma(2\gamma r_c) + 4\Gamma(1 + 2\gamma r_c)(-(1 + \gamma r_{b1})(C + \psi(2\gamma r_c) + \gamma r_c \psi'(2\gamma r_c)))]-$$

$$-2 r_c \Gamma(1 + 2\gamma r_c)[\Phi(e^{r_{b1}/r_c}, 1, 2\gamma r_c) + \ln(1 - e^{r_{b1}/r_c}) + \gamma r_c(\Phi(e^{r_{b1}/r_c}, 2, 2\gamma r_c) +$$

$$+Li_2(e^{r_{b1}/r_c}))]\Big).$$

The integral I_5 is similar to I_4 so that we present the final expression,

$$\int\limits_0^\infty dr_{b2}\ I_5 = -\frac{1}{8\gamma r_{b1}}\Big(3 + 4\gamma r_c[e^{-r_{b1}/r_c}(\Phi(e^{-r_{b1}/r_c}, 1, 1 + 2\gamma r_c) + \tag{3.76}$$

$$+\Phi(e^{-r_{b1}/r_c}, 2, 1 + 2\gamma r_c)) + \ln(1 - e^{r_{b1}/r_c}) - \gamma r_c \psi'(e^{r_{b1}/r_c})]\Big).$$

Now, we are in a position to sum up all the calculated integrals $I_1, \dots, I_5$, and obtain, due to (3.25), the following final expression for the Coloumb integral over coordinates of *second* electron,

$$I(r_{b1}) = -(\frac{1}{2} + \frac{5}{8\gamma r_{b1}})e^{-2\gamma r_{b1}} + \tag{3.77}$$

$$+\frac{1}{2}\gamma r_c\Big[\pi(1+\frac{1}{\gamma r_{b1}})\mathrm{ctg}(2\gamma r_c\pi)e^{-2\gamma r_{b1}} - \frac{1}{\gamma r_{b1}}e^{-r_{b1}/r_c}\Phi(e^{-r_{b1}/r_c},1,1+2\gamma r_c)+$$

$$+\Phi(e^{r_{b1}/r_c},1,-2\gamma r_c) - \Phi(e^{r_{b1}/r_c},1,2\gamma r_c) + \frac{1}{\gamma r_{b1}}\Phi(e^{r_{b1}/r_c},1,-2\gamma r_c)\Big]+$$

$$+\gamma^2 {r_c}^2\Big[-\frac{1}{2\gamma r_{b1}}e^{-r_{b1}/r_c}\Phi(e^{-r_{b1}/r_c},2,-2\gamma r_c) - \Phi(e^{r_{b1}/r_c},2,-2\gamma r_c)-$$

$$-\Phi(e^{r_{b1}/r_c},2,2\gamma r_c) + \frac{1}{\gamma r_{b1}}(\frac{1}{2}\Phi(e^{r_{b1}/r_c},2,2\gamma r_c) - \Phi(e^{r_{b1}/r_c},2,-2\gamma r_c))+$$

$$+\frac{1}{\gamma r_{b1}}e^{-2\gamma r_{b1}}\psi'(2\gamma r_c) + e^{-2\gamma r_{b1}}(1+\frac{1}{\gamma r_{b1}})(\zeta(2,-2\gamma r_c) - \zeta(2,2\gamma r_c))\Big]+$$

$$+\frac{2}{\gamma r_{b1}}\gamma^3 {r_c}^3\Big[\Phi(e^{r_{b1}/r_c},3,2\gamma r_c) + \Phi(e^{r_{b1}/r_c},3,-2\gamma r_c)-$$

$$-e^{-2\gamma r_{b1}}(\zeta(3,2\gamma r_c) + \zeta(3,-2\gamma r_c))\Big],$$

where we have collected the terms due to power degrees of r_c. It should be stressed that here $(2\gamma r_c)^{-1}$ is assumed to be an integer number. The above expression represents the Hulten part of the electrostatic potential caused by charge distribution of the second electron.

Next step is to integrate (3.77) over the coordinates of *first* electron,

$$\mathcal{C}'_h = 2\pi\int_0^\pi d\theta_1 \int_0^\infty dr_{b1}\ I(r_{b1})\frac{\gamma^3}{\pi}e^{-2\gamma\sqrt{{r_{b1}}^2+R^2-{r_{b1}}^2 R\cos\theta_1}}{r_{b1}}^2\sin\theta_1. \tag{3.78}$$

Prior to that, we denote

$$\lambda = 2\gamma r_c = \frac{1}{k}, \quad r = \gamma r_{b1}, \tag{3.79}$$

and rewrite Eq. (3.77) in a more compact form,

$$I(r) = -(\frac{1}{2}+\frac{5}{8r})e^{-2r}+\frac{1}{4}\lambda\Big[\pi(1+\frac{1}{r})\mathrm{ctg}(\pi\lambda)e^{-2r}-\frac{1}{r}e^{-2r/\lambda}\Phi(e^{-2r/\lambda},1,1+\lambda)+$$
$$(3.80)$$
$$+\Phi(e^{2r/\lambda},1,-\lambda)-\Phi(e^{2r/\lambda},1,\lambda)+\frac{1}{r}\Phi(e^{2r/\lambda},1,-\lambda)\Big]+$$
$$+\frac{\lambda^2}{4}\Big[-\frac{1}{2r}e^{-2r/\lambda}\Phi(e^{-2r/\lambda},2,-\lambda)-\Phi(e^{2r/\lambda},2,-\lambda)-\Phi(e^{2r/\lambda},2,\lambda)+$$
$$\frac{1}{r}(\frac{1}{2}\Phi(e^{2r/\lambda},2,\lambda)-\Phi(e^{2r/\lambda},2,-\lambda)+e^{-2r}\psi'(\lambda))+e^{-2r}(1+\frac{1}{r})(\zeta(2,-\lambda)-\zeta(2,\lambda))\Big]$$
$$+\frac{\lambda^3}{4r}\Big[\Phi(e^{2r/\lambda},3,\lambda)+\Phi(e^{2r/\lambda},3,-\lambda)-e^{-2r}(\zeta(3,\lambda)+\zeta(3,-\lambda))\Big].$$

Since $I(r)$ does not depend on θ_1 one can easily integrate over θ_1 in Eq.(3.78), and then change variable r_{b1} to $r=\gamma r_{b1}$, obtaining

$$\mathcal{C}_h' = \frac{1}{2\rho}\int\limits_0^\infty dr\ I(r)\Big[(1+2\sqrt{(\rho-r)^2})re^{-2\sqrt{(\rho-r)^2}}-(1+2(\rho+r))re^{-2(\rho+r)}\Big], \tag{3.81}$$

where $\rho=\gamma R$. Again, we should use separate intervals to keep $(\rho-r)$ to be positive, namely, we rewrite $\mathcal{C}_h'$ as

$$\mathcal{C}_h' = J_1+J_2+J_3, \tag{3.82}$$

where

$$J_1 = \frac{1}{2\rho}\int\limits_0^\rho dr\ I(r)(1+2\rho-2r)re^{-2(\rho-r)}, \tag{3.83}$$

$$J_2 = \frac{1}{2\rho}\int\limits_\rho^\infty dr\ I(r)(1+2r-2\rho)re^{-2(r-\rho)}, \tag{3.84}$$

$$J_3 = -\frac{1}{2\rho}\int\limits_0^\infty dr\ I(r)(1+2\rho+2r)re^{-2(\rho+r)}. \tag{3.85}$$

Now, we are ready to make integration over the last remaining variable, r, to obtain complete analytical expression of the Coloumb integral for the Hulten potential.

However, Lerch functions entering Eq.(3.80) make obstacle to do integral (3.82) for a general case because they have different functional form for different values of the parameter λ. So, each of the above integrals $J_{1,2,3}$ should be calculated independently for every numerical value of λ. Moreover, for the values of interest, e.g., $\lambda = 1/30$, *each* Lerch function is expressed in the form of sum of elementary functions with too big number of nontrivial terms to handle them (incomplete Euler beta function arises here). So, the integral cannot be reliably calculated even for a single value of λ, within the interval of interest, $\lambda = 1/30, 1/31, \ldots, 1/100$. Also, elementary analysis shows that we can not implement the assumption of small r_c into Eq.(3.80), to use first order approximation in r_c. Indeed, Lerch functions in (3.80) contain r_c both in first and third argument so that their asymptotics at $r_c \to 0$ make no sense.

Thus, we stop here further calculation of the Coloumb integral $\mathcal{C}'_h$ getting, however, as our main result the fact that $(2\gamma r_c)^{-1}$ should be integer number, in the variational approach to the model, to have finite energy of the ground state. We consider this as very interesting result deserving rather involved calculations made above.

Also, we have a detailed technical view on the problems which arise when dealing with molecular integrals with the Hulten potential. Practically, this means that there is a very little hope that the *exchange* integral (3.7), which is structurally much more complicated than the above considered Coloumb one, can be calculated exactly for the case of Hulten potential.

Because of these difficulties, below we use appropriate *simplified* potentials, instead of Hulten potential, to have some analytical set up for the variational analysis of the Santilli-Shillady model. Clearly, by this we go to some approximation to the original Santilli-Shillady model.

3.1.2 Coloumb integral for exponential screened Coloumb potential

We use simple function to mimic Hulten potential. Namely, we approximate the general potential (2.2) by

$$V(r_{12}) = V_C + V_e = \frac{e^2}{r_{12}} - \frac{Ae^{-r_{12}/r_c}}{r_{12}}, \tag{3.86}$$

where A and r_c are positive parameters. It has similar behavior both at short and long distances. Indeed, at long distances, $r_{12} \to \infty$, we can ignore V_e and the behavior is solely due to the Coloumb potential while its series expansion about the point $r_{12} = 0$ (short distances) is

$$V(r_{12})_{|r_{12}\to 0} = \frac{e^2 - A}{r_{12}} + \frac{A}{r_c} - \frac{A}{2r_c} r_{12} + O(r_{12}^2). \tag{3.87}$$

Here, we should put $A = V_0 r_c$ to have the same coefficient at r_{12}^{-1} in the $r_{12} \to 0$ asymptotics as it is in the case of Hulten potential; see Eq.(2.4). Using Eq.(3.21) we have

$$A = V_0 r_c = \frac{\beta^2 \hbar^2}{2 m r_c}, \quad \beta = 1, 2, \ldots, \tag{3.88}$$

where β is a number of energy levels of isoelectronium. Taking $\beta = 1$ we have, in atomic units ($\hbar = 1$, $m = m_e/2 = 1/2$),

$$A = \frac{1}{r_c}. \tag{3.89}$$

Below, we calculate the Coloumb integral (3.5), with the exponential screened Coloumb potential V_e defined by Eq.(3.86),

$$\mathcal{C}'_E = \int dv_1 dv_2 \, \left(\frac{e^2}{r_{12}} - \frac{A e^{-r_{12}/r_c}}{r_{12}} \right) |f(r_{a1})|^2 |f(r_{b2})|^2, \tag{3.90}$$

Below, we present some details of calculation of the Coloumb integral (3.90). Apart from the case of Hulten potential considered in Sec. 3.1.1, it appears that this integral can be calculated in terms of elementary functions.

The integral we are calculating is

$$\mathcal{C}'_e = \int dv_1 dv_2 \, \frac{A e^{-r_{12}/r_c}}{r_{12}} |f(r_{a1})|^2 |f(r_{b2})|^2, \tag{3.91}$$

where

$$f(r) = \sqrt{\frac{\gamma^3}{\pi}} e^{-\gamma r}, \tag{3.92}$$

and dv_1 and dv_2 are volume elements for the first and second electron, respectively. We use spherical coordinates. In spherical coordinates $(r_{b2}, \theta_2, \varphi_2)$, with polar axis directed along the vector $\vec{r}_{b1}$, we have

$$r_{12} = \sqrt{{r_{b1}}^2 + {r_{b2}}^2 - 2r_{b1}r_{b2}\cos\theta_2}. \tag{3.93}$$

We use these coordinates when integrating over second electron. In spherical coordinates $(r_{b1}, \theta_1, \varphi_1)$, with polar axis directed along the vector $\vec{R}$, we have

$$r_{a1} = \sqrt{{r_{b1}}^2 + R^2 - 2r_{b1}R\cos\theta_1}. \tag{3.94}$$

We use these coordinates when integrating over first electron.

First, we integrate over angular coordinates of second electron,

$$I_1 = \int_0^{2\pi} d\varphi_2 \int_0^{\pi} d\theta_2 \ \frac{Ae^{-r_{12}/r_c}}{r_{12}} \frac{\gamma^3}{\pi} e^{-2\gamma r_{b2}} {r_{b2}}^2 \sin\theta_2, \tag{3.95}$$

where r_{12} is defined by (3.93). It is relatively easy to calculate this integral,

$$I_1 = \frac{2A\gamma^3 r_c}{r_{b1}} e^{-2\gamma r_{b2}} \left(e^{-\sqrt{(r_{b2}-r_{b1})^2}/r_c} - e^{-\sqrt{(r_{b2}+r_{b1})^2}/r_c} \right). \tag{3.96}$$

Further, integrating on radial coordinate r_{b2} must be performed in separate intervals,

$$I_2 = \int_0^{r_{b1}} dr_{b2} \ I_1(r_{b2} < r_{b1}) + \int_{r_{b1}}^{\infty} dr_{b2} \ I_1(r_{b2} > r_{b1}), \tag{3.97}$$

where

$$\sqrt{(r_{b1} - r_{b2})^2} = \begin{cases} r_{b1} - r_{b2}, & r_{b2} < r_{b1}, \\ r_{b2} - r_{b1}, & r_{b2} > r_{b1}, \end{cases} \tag{3.98}$$

with the result

$$I_2 = \frac{4A\gamma^3 {r_c}^2 (4\gamma {r_c}^2 (e^{-r_{b1}/r_c} - e^{-2\gamma r_{b1}}) + r_{b1} e^{-2\gamma r_{b1}} (1 - 4\gamma^2 {r_c}^2))}{r_{b1}(1 - 4\gamma^2 {r_c}^2)^2}. \tag{3.99}$$

Now, we turn to integrating over coordinates of first electron, $(r_{b1}, \theta_1, \varphi_1)$,

$$I_3 = \int_0^{\pi} d\theta_1 \int_0^{2\pi} d\varphi_1 \ I_2 \frac{\gamma^3}{\pi} e^{-2\gamma r_{a1}} {r_{b1}}^2 \sin\theta_1, \tag{3.100}$$

where r_{a1} is defined by (3.94). We obtain after tedious calculations

$$I_3 = \frac{2A\gamma^4 {r_c}^2}{R(1-4\gamma^2{r_c}^2)^2} e^{-2\gamma(\sqrt{(R-r_{b1})^2}+r_{b1}+\sqrt{(R+r_{b1})^2})-r_{b1}/r_c} \tag{3.101}$$

$$\times \left[e^{2\gamma\sqrt{(R+r_{b1})^2}} - 2\gamma e^{2\gamma\sqrt{(R+r_{b1})^2}}\sqrt{(R-r_{b1})^2} + 2\gamma e^{2\gamma\sqrt{(R-r_{b1})^2}}\sqrt{(R+r_{b1})^2}\right]$$

$$\times \left[e^{r_{b1}/r_c}(4\gamma(1+\gamma r_{b1}){r_c}^2 - r_{b1}) - 4\gamma {r_c}^2 e^{2\gamma r_{b1}}\right].$$

Again, we must further integrate in r_{b1} by separate intervals,

$$I_4 = \int_0^R dr_{b1}\ I_3(r_{b1} < R) + \int_R^\infty dr_{b1}\ I_3(r_{b1} > R) \equiv I_{41} + I_{42}, \tag{3.102}$$

obtaining after rather tedious calculations

$$I_{41} = \frac{Ae^{-6\gamma R}\gamma^2{r_c}^2}{12R(1-4\gamma^2{r_c}^2)^4}\times \tag{3.103}$$

$$\Big[96e^{2\gamma R-R/r_c}\gamma^3\Big((4\gamma(2\gamma Rr_c+R+r_c)+1)(1-2\gamma r_c)^2+e^{4\gamma R}(2\gamma r_c+1)^2(4\gamma r_c-1)\Big){r_c}^3$$

$$-3e^{4\gamma R} + 3\gamma\Big(-64\gamma^5(\gamma R(8\gamma R+13)+4){r_c}^6 + 16\gamma^3(\gamma R(24\gamma R+31)+9){r_c}^4$$

$$-4\gamma(\gamma R(24\gamma R+23)+6){r_c}^2 + R(8\gamma R+5)\Big) - e^{4\gamma R}\gamma\times$$

$$\Big(64\gamma^5(\gamma R(4\gamma R(2\gamma R+9)+57)+36){r_c}^6 - 48\gamma^3(\gamma R(4\gamma R(2\gamma R+7)+21)-9){r_c}^4$$

$$+12\gamma(\gamma R(4\gamma R(2\gamma R+5)+1)-6){r_c}^2 - R(4\gamma R(2\gamma R+3)-3)+3)\Big)+3\Big],$$

$$I_{42} = -\frac{Ae^{-6\gamma R}\gamma^2{r_c}^2}{4R(1-2\gamma r_c)^2(1+2\gamma r_c)^4}\times \tag{3.104}$$

$$\times\Big[1 - e^{4\gamma R} - 128\gamma^6R^2{r_c}^5 + \gamma\Big((5-3e^{4\gamma R})R - 4(e^{4\gamma R}-1)r_c\Big)+$$

$$+16\gamma^5R{r_c}^3\Big(-8R + (16e^{2\gamma R-R/r_c}+3e^{4\gamma R}-13)r_c\Big)+$$

$$+16e^{-R/r_c}\gamma^4{r_c}^3\Big((8e^{2\gamma R}+3e^{4\gamma+R/r_c}-13e^{R/r_c}R-4(e^{4\gamma R}-1)(2e^{2\gamma R}-e^{R/r_c})r_c\Big)+$$

$$+4\gamma^2\Big(2R^2-(3e^{4\gamma R}-5)Rr_c+3(e^{4\gamma R}-1){r_c}^2\Big)+$$

$$+32\gamma^3 r_c\Big(R^2 - Rr_c + e^{-R/r_c}(e^{4\gamma R}-1)(2e^{R/r_c} - e^{2\gamma R}){r_c}^2)\Big)\Big].$$

In calculating I_{42}, we put the condition

$$6\gamma r_c < 1, \tag{3.105}$$

which is necessary to prevent divergency at the endpoint $r_{b1} = \infty$. Collecting the above two integrals we obtain

$$I_4 \equiv \mathcal{C}'_e = -\frac{A\gamma^3 {r_c}^2}{6R(1-4\gamma^2 {r_c}^2)^4}\Big[e^{-2\gamma R}\Big(-R(3+2\gamma R(3+2\gamma R)) \tag{3.106}$$
$$+12\gamma^2 R{r_c}^2(5+2\gamma R(5+2\gamma R)) - 48\gamma^4 R{r_c}^4(15+2\gamma R(7+2\gamma R))$$
$$+64\gamma^5 {r_c}^6(24+\gamma R(33+2\gamma R(9+2\gamma R)))\Big) - 1536\gamma^5 {r_c}^6 e^{-R/r_c}\Big].$$

Thus, we have finally for the Coloumb integral for exponential screened Coloumb potential,

$$\mathcal{C}'_e = -\frac{A\lambda^2}{8(1-\lambda^2)^4}\frac{\gamma e^{-2\rho}}{\rho}\Big[-(\rho+2\rho^2+\frac{4}{3}\rho^3) + 3\lambda^2(5\rho+10\rho^2+4\rho^3) \tag{3.107}$$
$$-\lambda^4(15\rho+14\rho^2+4\rho^3) + \lambda^6(8+11\rho+6\rho^2+\frac{4}{3}\rho^3 - 8e^{2\rho-\frac{2\rho}{\lambda}})\Big].$$

Here, we have used notation $\lambda = 2\gamma r_c$, and also $\lambda < 1/3$ due to Eq.(3.105).

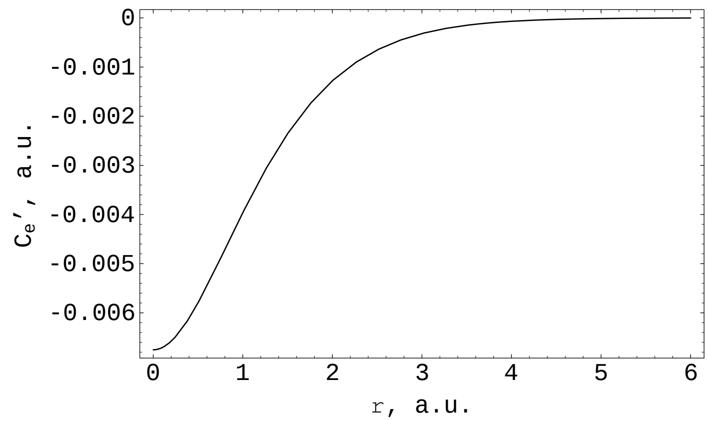

Figure 5: The Coloumb integral $\mathcal{C}_e'$ as a function of ρ, Eq. (3.107), at $\lambda = 1/37$. Here, $\rho = \gamma R$, where R is the internuclear distance, and $\lambda = 2\gamma r_c$, where r_c is the correlation length parameter.

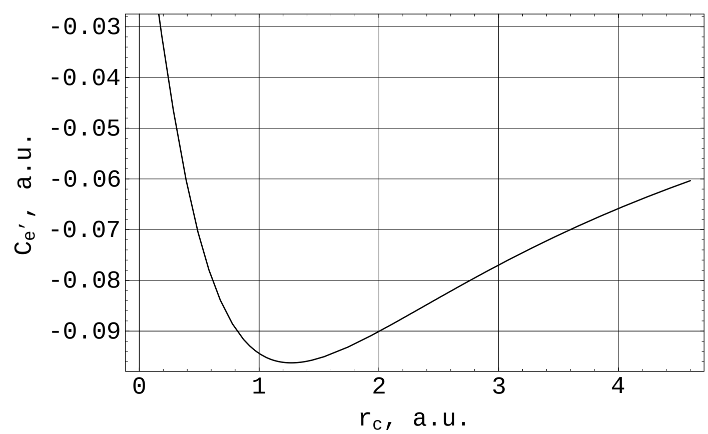

Figure 6: The Coloumb integral $\mathcal{C}_e'$ as a function of r_c, Eq. (3.107), at $\rho = 1.67$. For $r_c > 0.2$ a.u., the regularized values of $\mathcal{C}_e'$ are presented.

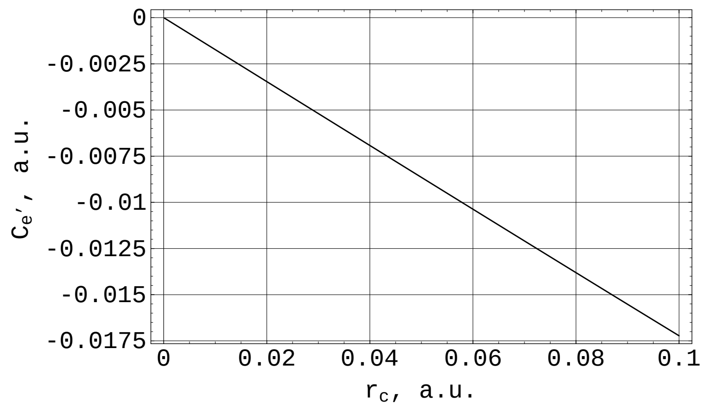

Figure 7: The Coloumb integral $\mathcal{C}'_e$ as a function of r_c, Eq. (3.107), at $\rho = 1.67$. More detailed view.

The total Coloumb integral is

$$\mathcal{C}'_E = \mathcal{C}'_C - \mathcal{C}'_e, \tag{3.108}$$

where $\mathcal{C}'_C$ is wellknown Coloumb potential part given by Eq.(3.13).

Below, we turn to the other potential, Gaussian screened Coloumb potential, considered by Santilli and Shillady [1]. The Coloumb integral for this potential can be calculated exactly, and the result contains one special function, the error function erf(z).

3.1.3 Coloumb integral for Gaussian screened Coloumb potential

In this Section, we calculate the Coloumb integral for the case of Gaussian screened potential. Namely, we approximate the general potential (2.2) by [1]

$$V(r_{12}) = V_C + V_g = \frac{e^2}{r_{12}} - \frac{Ae^{-r_{12}^2/c}}{r_{12}}, \tag{3.109}$$

where A and $c = {r_c}^2$ are positive parameters. At long distances, $r_{12} \to \infty$, we can ignore V_g while its series expansion about the point $r_{12} = 0$ is

$$V(r_{12})_{|r_{12}\to 0} = \frac{e^2 - A}{r_{12}} + \frac{A}{c} r_{12} + O(r_{12}^2). \tag{3.110}$$

Here, we should put $A = V_0 r_c$ to have the same coefficient at r_{12}^{-1} in the $r_{12} \to 0$ asymptotics as it is in the case of Hulten potential; see Eq.(2.4).

The Coloumb integral is

$$\mathcal{C}'_G = \int dv_1 dv_2 \, \left(\frac{e^2}{r_{12}} - \frac{Ae^{-r_{12}^2/c}}{r_{12}} \right) |f(r_{a1})|^2 |f(r_{b2})|^2. \tag{3.111}$$

The integral we are calculating is

$$\mathcal{C}'_g = \int dv_1 dv_2 \, \frac{Ae^{-r_{12}^2/c}}{r_{12}} |f(r_{a1})|^2 |f(r_{b2})|^2, \tag{3.112}$$

where notation and coordinate system are due to Sec. 3.1.2. First, we integrate over angular coordinates of second electron,

$$I_1 = \int\limits_0^{2\pi} d\varphi_2 \int\limits_0^{\pi} d\theta_2 \, \frac{Ae^{-r_{12}^2/c}}{r_{12}} \frac{\gamma^3}{\pi} e^{-2\gamma r_{b2}} {r_{b2}}^2 \sin\theta_2, \tag{3.113}$$

where r_{12} is defined by (3.93). We have

$$I_1 = \frac{A\gamma^3 \sqrt{\pi c} e^{-2\gamma r_{b2}}}{r_{b1}} \left(\mathrm{erf}(\sqrt{\frac{(r_{b1}+r_{b2})^2}{c}}) - \mathrm{erf}(\sqrt{\frac{(r_{b1}-r_{b2})^2}{c}}) \right), \tag{3.114}$$

where

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int\limits_0^z e^{-t^2} dt \tag{3.115}$$

is error function. Further, integrating on radial coordinate r_{b2} must be performed in separate intervals,

$$I_2 = \int\limits_0^{r_{b1}} dr_{b2} \; I_1(r_{b2} < r_{b1}) + \int\limits_{r_{b1}}^{\infty} dr_{b2} \; I_1(r_{b2} > r_{b1}), \tag{3.116}$$

where

$$\sqrt{(r_{b1}-r_{b2})^2} = \begin{cases} r_{b1}-r_{b2}, & r_{b2} < r_{b1}, \\ r_{b2}-r_{b1}, & r_{b2} > r_{b1}, \end{cases} \tag{3.117}$$

with the result

$$I_2 = -\frac{A\gamma\sqrt{c}e^{-2\gamma r_{b1}-{r_{b1}}^2/c}}{4r_{b1}}\Bigg(4\gamma\sqrt{c}(e^{{r_{b1}}^2/c}-e^{2\gamma r_{b1}}) \tag{3.118}$$

$$+\sqrt{\pi}e^{{r_{b1}}^2/c+c\gamma^2}\Bigg[(1+2\gamma(r_{b1}-c\gamma))(\mathrm{erfc}(\frac{r_{b1}-c\gamma}{\sqrt{c}})+2\mathrm{erfc}(\sqrt{c}\gamma)-2)$$

$$+e^{4\gamma r_{b1}}(2\gamma(r_{b1}+c\gamma)-1)\mathrm{erfc}(\frac{r_{b1}+c\gamma}{\sqrt{c}})\Bigg]\Bigg),$$

where $\mathrm{erfc}(z) = 1-\mathrm{erf}(z)$. Now, we turn to integrating over coordinates of first electron, $(r_{b1},\theta_1,\varphi_1)$,

$$I_3 = \int_0^{\pi} d\theta_1 \int_0^{2\pi} d\varphi_1 \; I_2\frac{\gamma^3}{\pi}e^{-2\gamma r_{a1}}{r_{b1}}^2\sin\theta_1, \tag{3.119}$$

where r_{a1} is defined by (3.94). We obtain after tedious calculations

$$I_3 = -\frac{A\sqrt{c}\gamma^2}{8R}e^{-\frac{{r_{b1}}^2}{c}-2\gamma(\sqrt{(R-r_{b1})^2}+2r_{b1}+\sqrt{(R+r_{b1})^2})} \tag{3.120}$$

$$\times\Bigg(e^{2\gamma(\sqrt{(R-r_{b1})^2}+r_{b1})}-e^{2\gamma(\sqrt{(R+r_{b1})^2}+r_{b1})}-2\gamma e^{2\gamma(\sqrt{(R+r_{b1})^2}+r_{b1})}\sqrt{(R-r_{b1})^2}$$

$$+2\gamma e^{2\gamma(\sqrt{(R-r_{b1})^2}+r_{b1})}\sqrt{(R+r_{b1})^2}\Bigg)$$

$$\times\Bigg[\sqrt{\pi}e^{\frac{{r_{b1}}^2}{c}+c\gamma^2}\Bigg((1+2\gamma r_{b1}-2c\gamma^2)(2\mathrm{erfc}(\gamma\sqrt{c})+\mathrm{erfc}(\frac{r_{b1}-\gamma c}{\sqrt{c}})-2)$$

$$+(1+2\gamma r_{b1}+2c\gamma^2)e^{4\gamma r_{b1}}\mathrm{erfc}(\frac{r_{b1}+\gamma c}{\sqrt{c}})\Bigg)\Bigg].$$

Again, we must further integrate in r_{b1} by separate intervals,

$$I_4 = \int_0^{R} dr_{b1}\; I_3(r_{b1}<R) + \int_R^{\infty} dr_{b1}\; I_3(r_{b1}>R). \tag{3.121}$$

First, we replace the endpoint $r_{b1} = \infty$ by finite value $r_{b1} = \Lambda$ to avoid divergencies at intermediate calculations. After straightforward but tedious calculations we obtain rather long expression so that we do not represent it here noting however that the following integrals are used during the calculations:

$$\int \mathrm{erf}(z)dz = \frac{e^{-z^2}}{\sqrt{\pi}} + z\ \mathrm{erf}(z), \tag{3.122}$$

$$\int z\ \mathrm{erf}(z)dz = \frac{ze^{-z^2}}{2\sqrt{\pi}} - \frac{1}{4}\mathrm{erf}(z) + \frac{1}{2}z^2\mathrm{erf}(z), \tag{3.123}$$

$$\int e^{-az}\mathrm{erf}(z)dz = -\frac{1}{a}e^{-az}\mathrm{erf}(z) + \frac{1}{a}e^{a^2/4}\mathrm{erf}(\frac{a}{2} + z), \tag{3.124}$$

$$\int ze^{-az}\mathrm{erf}(z)dz = -\frac{1}{a\sqrt{\pi}}e^{-az-z^2} - \frac{1}{a^2}e^{-az}(1+az)\mathrm{erf}(z) \tag{3.125}$$

$$-\frac{1}{2a^2}(a^2-1)e^{a^2/4}\mathrm{erf}(\frac{a}{2}+z),$$

$$\int e^{-az-bz^2}dz = \frac{\sqrt{\pi}}{2\sqrt{b}}e^{a^2/(4b)}\mathrm{erf}(\frac{a+2bz}{2\sqrt{b}}), \tag{3.126}$$

$$\int ze^{-az-bz^2}dz = -\frac{1}{2b}e^{-az-bz^2} - \frac{a\sqrt{\pi}}{4b^{3/2}}e^{a^2/(4b)}\mathrm{erf}(\frac{a+2bz}{2\sqrt{b}}). \tag{3.127}$$

Using $\lim_{\Lambda\to\infty}\mathrm{erf}(\Lambda) = 1$ and replacing welldefined exponentially decreasing terms by zero, we obtain some finite terms and big number (about fourty) of Λ dependent terms, which are unbounded at $\Lambda \to \infty$. All the divergent terms totally cancel each other so the final expression turns out to be automatically finite.

As the result, we obtain the Coloumb integral for Gaussian screened Coloumb potential in the following form:

$$\mathcal{C}'_g = \frac{A\gamma\kappa e^{-2\rho}}{96\rho}\Big[-(60+96\rho+48\rho^2)\kappa + (32+48\rho)\kappa^3 - 16\kappa^5 \tag{3.128}$$

$$+\Big((60+16\rho^2)\kappa - 32\kappa^3 + 16\kappa^5\Big)e^{2\rho-\frac{\rho^2}{\kappa^2}}$$

$$+\sqrt{\pi}e^{\kappa^2}\Big((30\rho+8\rho^3-36\rho\kappa^2+24\rho\kappa^4)(2\mathrm{erf}(\kappa)-\mathrm{erfc}(\frac{\rho}{\kappa}-\kappa)-e^{4\rho}\mathrm{erfc}(\frac{\rho}{\kappa}+\kappa))$$

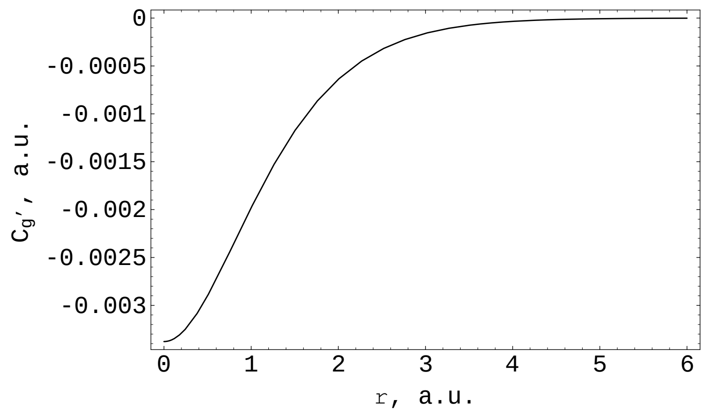

Figure 8: The Coloumb integral $\mathcal{C}'_g$ as a function of ρ, Eq. (3.128), at $2\kappa = \lambda = 1/37$. Here, $\rho = \gamma R$, where R is the internuclear distance, and $\lambda = 2\gamma r_c$, where r_c is the correlation length parameter.

$$+(15+24\rho^2-(18+24\rho^2)\kappa^2+12\kappa^4-8\kappa^6)(2\mathrm{erf}(\kappa)-\mathrm{erfc}(\frac{\rho}{\kappa}-\kappa)+e^{4\rho}\mathrm{erfc}(\frac{\rho}{\kappa}+\kappa))\Big)\Big],$$

where we have used notation

$$\kappa = \gamma\sqrt{c} = \gamma r_c = \frac{\lambda}{2}. \tag{3.129}$$

The total Coloumb integral is

$$\mathcal{C}'_G = \mathcal{C}'_C - \mathcal{C}'_g, \tag{3.130}$$

where $\mathcal{C}'_C$ is given by Eq.(3.13).

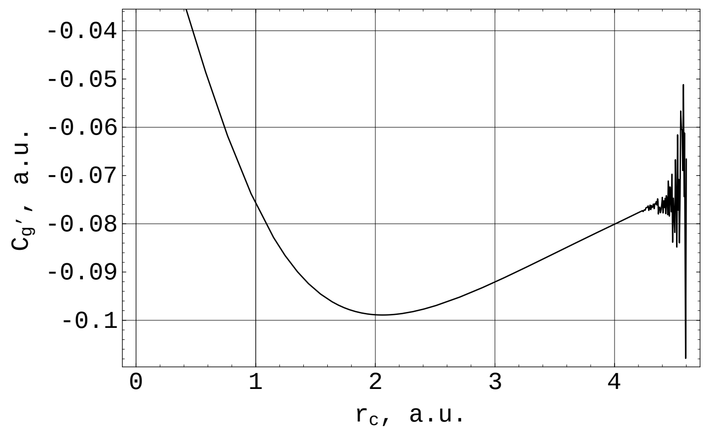

Figure 9: The Coloumb integral $\mathcal{C}_g'$ as a function of r_c, Eq. (3.128), at $\rho = 1.67$.

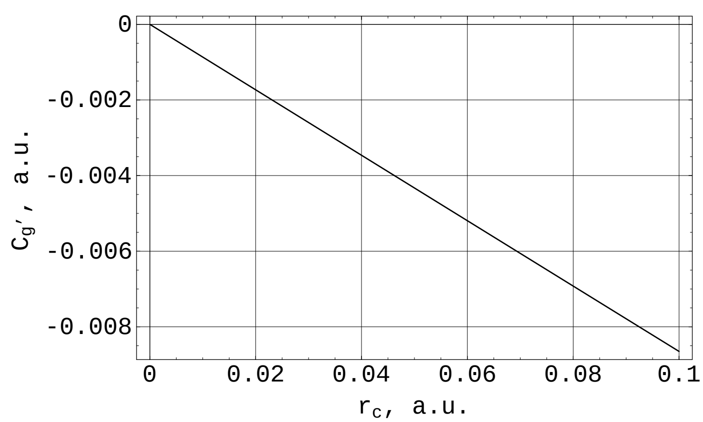

Figure 10: The Coloumb integral $\mathcal{C}_g'$ as a function of r_c, Eq. (3.128), at $\rho = 1.67$. More detailed view.

3.1.4 Exchange integral

Our general remark is that all calculations for the above *Coloumb* integrals are made in spherical coordinates, which correspond to spherical symmetry of the charge distributions of both $1s$ electrons, $|\psi(r_{a1})|^2$ and $|\psi(r_{a2})|^2$, each moving around one nucleus. One can use prolate spheroidal coordinates, which are exploited sometimes when integrating over coordinates of last electron, but we have encountered the same problem of big number of terms in the intermediate expressions, with no advantage in comparison to the use of spherical coordinates.

Unlike to Coloumb integral, calculation of *exchange* integral should be made in the spheroidal coordinates, which correspond to spheroidal symmetry of charge distributions of the electrons, $\psi^*(r_{a1})\psi(r_{b1})$ and $\psi^*(r_{a2})\psi(r_{b2})$, each moving around *both* the nuclei, a and b.

Calculation of the exchange integral,

$$\mathcal{E}' = \int dv_1 dv_2 \; V(r_{12}) f^*(r_{a1}) f(r_{b1}) f^*(r_{a2}) f(r_{b2}), \tag{3.131}$$

essentially depends on the form of the potential $V(r_{12})$ in the sense that the integration can be made only in *spheroidal* coordinates, (x_1, y_1, φ_1) and (x_2, y_2, φ_2), and one should use an expansion of $V(r_{12})$ in the associated Legendre polynomials.

For the usual Coloumb potential, $V(r_{12}) = r_{12}^{-1}$, it is rather long (about 12 pages to present the main details) and nontrivial calculation, where Neumann expansion in terms of associated Legendre polynomials, in spheroidal coordinates, is used (celebrated result by Sugiura, see Eq.(3.15)).

In general, any analytical square integrable function can be expanded in associated Legendre polynomials. However, in direct calculating of the expansion coefficients by means of integral of the function with Legendre polynomials, one meets serious problems even for simple functions. Practically, one uses, instead, properties of special functions to derive such expansions.

We mention that there is Gegenbauer expansion [6], having in a particular case the form [5]

$$\frac{e^{ikr_{12}}}{r_{12}} = \frac{1}{r_1 r_2} \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}} \frac{i}{k} j_l(kr_1) n_l^{(1)}(kr_2) Y_{l,0}(\theta_{12}), \tag{3.132}$$

where $j_l(z)$ and $n_l^{(1)}(z)$ are spherical Bessel and spherical Hankel functions of first kind, respectively, θ_{12} is angle between vectors $\vec{r}_1$ and $\vec{r}_2$, and $r_1 = |\vec{r}_1|$,

$r_2 = |\vec{r}_2|$; $r_1 < r_2$. Spherical harmonics $Y_{l,0}(\theta_{12})$ can be rewritten in terms of Legendre polynomials due to the summation theorem.

We note that this expansion can be used, at $k = i/r_c$, to reproduce exponential screened potential, $V_e(r_{12})$, and to calculate associated exchange integral (3.131) but, however, it concerns *spherical* (not spheroidal) coordinates, $(r_1, \theta_1, \varphi_1)$ and $(r_2, \theta_2, \varphi_2)$.

For Hulten potential $V_h(r_{12})$, exponential screened potential, $V_e(r_{12})$, and Gaussian screened potential, $V_g(r_{12})$, which are of interest in this paper, we have no such an expansion in *spheroidal* coordinates. To stress that this is not only the problem of changing coordinate system, we mention that the solution of usual 3-dimensional wave equation, $\Delta\psi + k^2\psi = 0$, is given by function $e^{i\vec{k}\vec{r}}/r$, in spherical coordinates, to which one can apply Gegenbauer expansion, while in spheroidal coordinates its solution is represented by complicated function containing infinite series of recurrent coefficients [7]; see also [4], Sec. 3.4. As the result, we have no possibility to calculate exactly exchange integrals for these non-Coloumb potentials.

In order to obtain *approximate* expression for the exchange integral for the case of the above non-Coloumb potentials, we make analysis of asymptotics of the standard exchange integral (i.e. that for the Coloumb potential), Eq.(3.15). It is easy to derive that

$$\mathcal{E}'_{C|\rho\to\infty} \sim e^{-2\rho}, \tag{3.133}$$

at long distances between the nuclei, and

$$\mathcal{E}'_{C|\rho=0} = \frac{5}{8}\gamma, \tag{3.134}$$

in the case of coinciding nuclei. At $r_c^{-1} \to 0$, we should have the same asymptotics for exchange integral for each of the above non-Coloumb potentials because these potentials behave as Coloumb potential at $r_c^{-1} \to 0$.

In both the limiting cases, $\rho \to \infty$ and $\rho = 0$, the exchange integral for the non-Coloumb potentials is simplified, and one can use spherical coordinates since the two-center problem is reduced to one-center problem. We consider two limiting cases.

a) $\rho = \infty$ case.

This case is trivial because exchange integral tends to zero due to lack of overlapping of the wave functions of two H atoms.

b) $\rho = 0$ case.

In this case , we have $r_{a1} = r_{b1} = r_1$ and $r_{a2} = r_{b2} = r_2$ so that Eq.(3.131) becomes

$$\mathcal{E}' = \int dv_1 dv_2 \; V(r_{12})|f(r_1)|^2|f(r_2)|^2, \tag{3.135}$$

One can see that this is the case of He atom with two electrons in the ground state. Evidently, in terms of our anzatz (3.1) we have complete overlapping of the wave functions.

Even the above mentioned simplification of the exchange integral and use of spherical coordinates does not enable us to calculate *straightforwardly* the integral (3.135) for the non-Coloumb potentials, V_h, V_e, or V_g; the integrands are still too complicated. This indicates that we should use expansion of these potentials in Legendre polynomials, in spherical coordinates, to perform the integrals. Only exponential screened potential V_e is given such an expansion here. Namely, this is Gegenbauer expansion (3.132), owing to which we can calculate the exchange potential for exponential screened potential V_e, to which we turn below.

Exchange integral for the exponential screened Coloumb potential V_e, at $\rho = 0$.

The integral is

$$\mathcal{E}'_{E|\rho=0} \equiv (\mathcal{E}'_C - \mathcal{E}'_e)_{|\rho=0} = \frac{5}{8}\gamma - \int dv_1 dv_2 \; \frac{Ae^{-r_{12}/r_c}}{r_{12}}|f(r_1)|^2|f(r_2)|^2, \tag{3.136}$$

where we have used Eq.(3.134) for the usual Coloumb potential part of the integral. In the Gegenbauer expansion (3.132), we assume $k = i/r_c$ to reproduce the potential $V_e(r_{12})$. Since the wave functions $f(r_1)$ and $f(r_2)$ given by Eq.(3.10) do not depend on the angles, only $l = 0$, $m = 0$ term of the expansion (3.132) contributes to the exchange integral (3.136) due to orthogonality of Legendre polynomials. Using

$$j_0(z) = \sin z, \quad n_0(z) = -ie^{iz}, \quad Y_{0,0} = \sqrt{\frac{1}{4\pi}}, \tag{3.137}$$

we thus have

$$\frac{Ae^{ikr_{12}}}{r_{12}} \to \begin{cases} \frac{A}{kr_1r_2} \sin kr_1 e^{ikr_2}, & r_1 < r_2, \\ \frac{A}{kr_1r_2} \sin kr_2 e^{ikr_1}, & r_1 > r_2, \end{cases} \tag{3.138}$$

Then the exchange integral (3.136) is written as

$$\mathcal{E}'_{E|\rho=0} = \frac{5}{8}\gamma - \int_0^\infty 4\pi r_2^2 dr_2 \Big[\int_0^{r_2} 4\pi r_1^2 dr_1 \frac{A}{kr_1 r_2} \sin kr_1 e^{ikr_2} \frac{\gamma^3}{\pi} e^{-2\gamma r_1} \frac{\gamma^3}{\pi} e^{-2\gamma r_2}$$

$$+ \int_{r_2}^\infty 4\pi r_1^2 dr_1 \frac{A}{kr_1 r_2} \sin kr_2 e^{ikr_1} \frac{\gamma^3}{\pi} e^{-2\gamma r_1} \frac{\gamma^3}{\pi} e^{-2\gamma r_2}\Big], \tag{3.139}$$

where $4\pi r_1^2$ and $4\pi r_2^2$ are volume factors. The two above integrals over r_1 can be easily calculated, with the result

$$\frac{16A\gamma^6 r_2}{(k^2+4\gamma^2)^2}\Big[4\gamma e^{i(k+2i\gamma)r_2} + \frac{1}{k} e^{i(k+4i\gamma)}\Big((k^2-4\gamma^2)\sin kr_2 - 4k\gamma\cos kr_2 \tag{3.140}$$

$$-(k^2+4\gamma^2)(k\cos kr_2 + 2\gamma\sin kr_2)\Big)\Big]$$

and

$$-\frac{16A\gamma^6 r_2}{k(k+2i\gamma)^2}\Big(1 + (2\gamma - ik)\sin kr_2 e^{i(k+4i\gamma)}\Big). \tag{3.141}$$

Summing up these terms and integrating over r_2 we get after some algebra

$$\mathcal{E}'_{E|\rho=0} = \frac{5}{8}\gamma + \frac{A\gamma^3}{2(k+2i\gamma)^4}(k^2 + 8ik\gamma - 20\gamma^2). \tag{3.142}$$

Inserting

$$k = \frac{i}{r_c}, \tag{3.143}$$

to reproduce the potential V_e, and denoting $\lambda = 2\gamma r_c$ we write down our final result,

$$\mathcal{E}'_{E|\rho=0} = \frac{5}{8}\gamma - \frac{\gamma A\lambda^2}{8(1+\lambda)^4}(1 + 4\lambda + 5\lambda^2). \tag{3.144}$$

Note that, at $r_c^{-1} \to 0$, i.e. at $\lambda \to \infty$, we have

$$\mathcal{E}'_{E|\rho=0} = \frac{5}{8}\gamma - \frac{5}{8}A\gamma \tag{3.145}$$

that is in agreement with the value (3.134). We should to emphasize here that Eq.(3.144) is *exact* result for the exchange integral $\mathcal{E}'_E$, at $\rho = 0$.

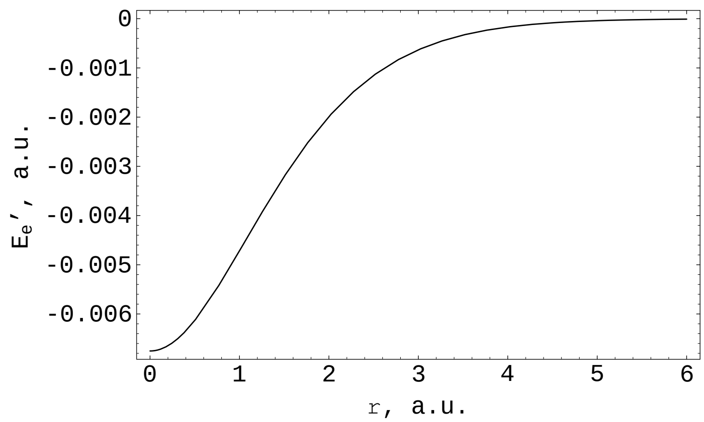

Figure 11: The exchange integral $\mathcal{E}_e'$ as a function of ρ, Eq. (3.146), at $\lambda = 1/37$. Here, $\rho = \gamma R$, where R is the internuclear distance, and $\lambda = 2\gamma r_c$, where r_c is the correlation length parameter.

Next step is to implement ρ dependence into (3.144) following to natural criteria. To restore partially ρ dependence in the exchange integral (3.144), we use exact result (3.15), and write down for the ρ dependent exchange integral the following *approximate* expression:

$$\mathcal{E}_E' = \mathcal{E}_C' - \mathcal{E}_e' \approx \mathcal{E}_C' - \frac{A\lambda^2}{(1+\lambda)^4}(\frac{1}{8} + \frac{1}{2}\lambda + \frac{5}{8}\lambda^2)\frac{8}{5}\mathcal{E}_C', \tag{3.146}$$

where $\mathcal{E}_C'$ is standard exact exchange integral for Coloumb potential given by Eq.(3.15) while the approximate λ dependent part arised from our potential V_e.

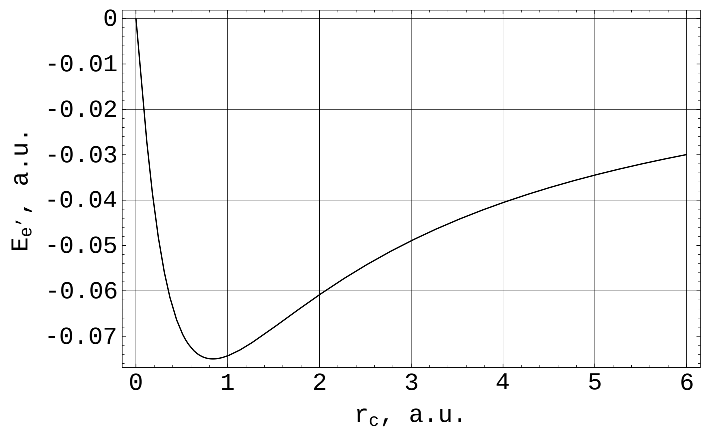

Figure 12: The exchange integral $\mathcal{E}_e'$ as a function of r_c, Eq. (3.146), at $\rho = 1.67$.

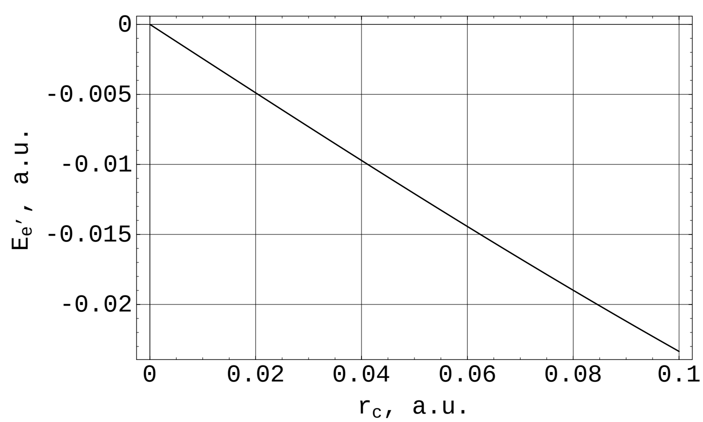

Figure 13: The exchange integral $\mathcal{E}_e'$ as a function of r_c, Eq. (3.146), at $\rho = 1.67$. More detailed view.

We have a good accuracy of the approximation (3.146). Indeed, exchange integrals make sensible contribution to the total molecular energy at deep overlapping of the wave functions, $S > 0.5$, and we have made calculation just for the case of complete overlapping, $S = 1$, with the necessary asymptotic factor, $e^{-2\rho}$, provided by $\mathcal{E}'_C(\rho)$. Note that at $\lambda \to \infty$, the term $\mathcal{E}'_e$ of Eq.(3.146) becomes $A\mathcal{E}'_C$, as it should be because at $\lambda \to \infty$ (no screening) we have $V_e \to A/r_{12}$. In addition, although there is no possibility to restore completely ρ dependence for the second term in r.h.s. of Eq.(3.146), we have got information on λ dependence, which is of *most* interest here.

3.2 Numerical calculations for the V_e-based model

In this Section, we consider the case of exponential screened potential $V_e = Ae^{-r_{12}/r_c}/r$, for which we have calculated all the needed molecular integrals.

The H_2 molecule energy, due to Eq.(3.2), is written as

$$E_{mol}(\gamma, R, A, r_c) = 2\frac{\mathcal{A} + \mathcal{A}'\mathcal{S}}{1 + \mathcal{S}^2} - \frac{2(\mathcal{C} + \mathcal{E}\mathcal{S}) - (\mathcal{C}'_C - \mathcal{C}'_e + \mathcal{E}'_C - \mathcal{E}'_e)}{1 + \mathcal{S}^2} + \frac{1}{R}, \tag{3.147}$$

where the specific terms are the Coloumb integral $\mathcal{C}'_e$ given by Eq.(3.107) and the exchange integral $\mathcal{E}'_e$ given by (3.146). We should find extremum of E_{mol} as a function of our basic parameters, γ, R, A, and r_c. We are using notation $\rho = \gamma R$ and $\lambda = 2\gamma r_c$ so that our four parameters are γ, ρ, A, and λ. In general, the number of energy levels of isoelectronium can also be viewed as a parameter of the model. However, we restrict our consideration by the one-level case, $\beta^2 = 1$; see Sec. 2.1.

3.2.1 Minimization of the energy

First, we analyze the A dependence of E_{mol}. Due to Eq.(3.89), for *one-level* isoelectronium we have $A = r_c^{-1}$, that can be identically rewritten as

$$A = \frac{2\gamma}{\lambda}. \tag{3.148}$$

Thus the A dependence converts to γ and λ dependence. This is the consequence of consideration of the Hulten potential interaction for the electron pair made in Sec. 2.1.

Second, we turn to γ dependence. Due to (3.148), the A dependent parts, $\mathcal{C}'_e$ and $\mathcal{E}'_e$, acquire additional γ factor and thus become γ^2 dependent. The other molecular integrals depend on γ linearly so that we define accordingly,

$$\bar{\mathcal{C}} = \frac{1}{\gamma}\mathcal{C}, \quad \bar{\mathcal{E}} = \frac{1}{\gamma}\mathcal{E}, \quad \bar{\mathcal{C}}'_C = \frac{1}{\gamma}\mathcal{C}'_C, \quad \bar{\mathcal{E}}'_C = \frac{1}{\gamma}\mathcal{E}'_C, \quad \bar{\mathcal{C}}'_e = \frac{1}{\gamma^2}\mathcal{C}'_e, \quad \bar{\mathcal{E}}'_e = \frac{1}{\gamma^2}\mathcal{E}'_e. \tag{3.149}$$

Inserting the computed integrals $\mathcal{A}$ and $\mathcal{A}'$ into (3.147) we have

$$E_{mol}(\gamma, \rho, \lambda) = -a\gamma + b\gamma^2, \tag{3.150}$$

where

$$a(\rho, \lambda) = \frac{2 + 2\bar{\mathcal{C}} + 4S\bar{\mathcal{E}} - \bar{\mathcal{C}}'_C - \bar{\mathcal{E}}'_C}{1 + S^2} - \frac{1}{\rho} \tag{3.151}$$

and

$$b(\rho, \lambda) = \frac{S^2 - 1 - 2S\bar{\mathcal{E}} + \bar{\mathcal{C}}'_e + \bar{\mathcal{E}}'_e}{1 + S^2}. \tag{3.152}$$

The value of γ corresponding to an extremum of E_{mol} is found from the equation $dE_{mol}/d\gamma = 0$, which gives the optimal value

$$\gamma_{opt} = \frac{a}{2b}. \tag{3.153}$$

Inserting this into (3.150) we get the extremal value of E_{mol},

$$E_{mol}(\rho, \lambda) = -\frac{a^2}{4b}. \tag{3.154}$$

Using definitions of a and b we have explicitly

$$\gamma_{opt} = \frac{1 - 2\rho + S^2 + \rho(-2\bar{\mathcal{C}} - 4S\bar{\mathcal{E}} + \bar{\mathcal{C}}'_C + \bar{\mathcal{C}}'_C)}{2\rho(-1 + S^2 - 2S\bar{\mathcal{E}}'_C + \bar{\mathcal{C}}'_e + \bar{\mathcal{E}}'_e)} \tag{3.155}$$

and

$$E_{mol}(\rho, \lambda) = \frac{(1 - 2\rho + S^2 + \rho(-2\bar{\mathcal{C}} - 4S\bar{\mathcal{E}} + \bar{\mathcal{C}}'_C + \bar{\mathcal{C}}'_C))^2}{4\rho^2(1 + S^2)(-1 + S^2 - 2S\bar{\mathcal{E}}'_C + \bar{\mathcal{C}}'_e + \bar{\mathcal{E}}'_e)}. \tag{3.156}$$

Next, we turn to the extremum in the parameter ρ. The ρ dependence, as well as the λ dependence, of E_{mol} is essentially nonalgebraic so that we are forced to use numerical calculations.

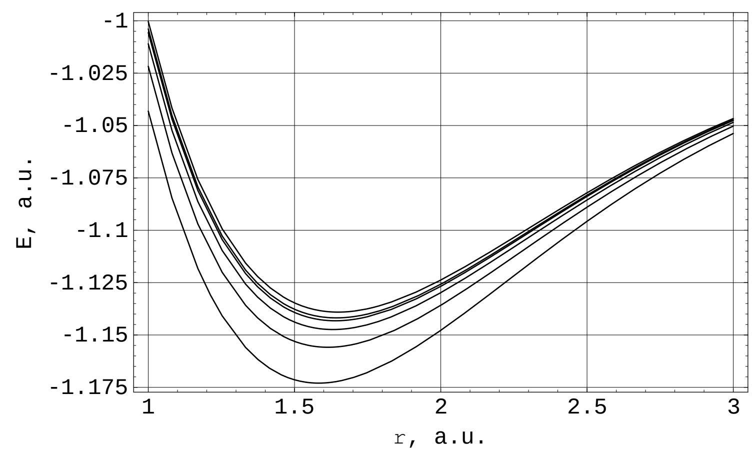

Figure 14: The total energy $E = E_{mol}$ as a function of ρ, Eq. (3.156), at $\lambda = 1/60, 1/40, 1/20, 1/10, 1/5$. The lowest plot corresponds to $\lambda = 1/5$ ($\rho = \gamma R$, $\lambda = 2\gamma r_c$).

It appears that the λ dependence does not reveal any local energy minimum while the ρ dependence does. Below, we use the condition, $\lambda^{-1} =$ *integer number*, obtained during the calculation of the Coloumb integral with Hulten potential V_h; see Eq.(3.57). Although there is obviously no necessity to keep this condition for the case of exponential screened potential V_e, we consider it as a prescription for allowed values of λ.

Since the λ dependence of the energy has no minimum we can use fitting of the predicted energy $E_{mol}(\lambda)$ to the experimental value by varying λ. This allows us to estimate the value of the parameter λ, and thus the value of the effective radius of the isoelectronium $r_c = \lambda/2\gamma_{opt}$.

3.2.2 Fitting of the energy and the bond length

The procedure is the following. We fix some numerical value of λ, and identify minimal value of $E_{mol}(\rho, \lambda)$, given by Eq.(3.156), in respect with the parameter ρ. This gives us minimal energy and corresponding optimal value of ρ, at some fixed value of λ. Then, we calculate γ_{opt} by using Eq.(3.155), and use obtained values of ρ_{opt} and γ_{opt} to calculate values of R_{opt} and r_c.

We calculated minimal values of E_{mol} in ρ, for a wide range of integer values of λ^{-1}. The results are presented in Tables 2 and 3, and Figures 15 and 16. One can see that the energy E_{mol} decreases with the increase of r_c (proportional to size of isoelectronium), as it was expected to be.

We note that all the presented values of E_{mol} in Tables 2 and 3 are lower than that, $E_{mol}^{var} = -1.139$ a.u., obtained via two-parametric Ritz variational approach to the standard model of H_2 (see, e.g., [5]), which is the model without the assumption of short-range attractive potential between the electrons. This means that the V_e-based model gives better prediction than the one of the standard model, for any admitted value of the effective radius of isoelectronium $r_c > 0$. Indeed, the standard prediction $E_{mol}^{var} = -1.139$ a.u. is much higher than the experimental value $E_{exper}[H_2] = -1.174474$ a.u.

3.2.3 The results of fitting

Best fit of the energy E_{mol}.

Due to Table 2 (see also Fig. 15), the experimental value, $E_{exp}[H_2] = -1.174... - 1.164$ a.u. (here we take 0.9% uncertainty of the experimental value) is fitted by

$$r_c = 0.0833...0.0600 \text{ a.u.}, \tag{3.157}$$

i.e. $\lambda = 1/5...1/7$, with the optimal distance, $R_{opt} = 1.3184...1.3441$ a.u. We see that the predicted R_{opt} appeared to be about 6% less than the experimental value $R_{exper}[H_2] = 1.4011$ a.u. We assign this discrepancy to the approximation we have made for the exchange integral (3.146).

Below we fit R_{opt}, to estimate the associated minimal energy.

Best fit of the internuclear distance R.

Due to Table 2 (see also Fig. 16), the experimental value of the internuclear distance, $R_{exp} = 1.4011$ a.u., is fitted by $r_c = 0.0115$ a.u., with the corresponding minimal energy $E_{min} = -1.144$ a.u., which is about 3% bigger than the experimental value. Again, we assign this discrepancy to the approximation we have made for the exchange integral (3.146), and take

$$r_c = 0.0115 \text{ a.u.}, \tag{3.158}$$

i.e. $\lambda = 1/37$, as the result of our final fit noting that (a) in ref. [1] the value $r_c = 0.0112$ a.u. has been used to make exact numerical fit of the energy, with corresponding $R = 1.40$ a.u., and (b) we have less discrepancy.

The weight of the pure isoelectronium phase.

To estimate the weight of the pure isoelectronium phase, which can be viewed as a measure of stability of the pure isoelectronium state, we use the above obtained fits and the fact that this phase makes contribution to the total molecular energy via the Coloumb and exchange integrals.

According to Eq.(3.147), the isoelectronium phase displays itself only by the term $P_e \equiv |\mathcal{C}'_e(\gamma,\rho,\lambda) + \mathcal{E}'_e(\gamma,\rho,\lambda)|$ while the Coloumb phase displays itself by the corresponding term $P_C \equiv |\mathcal{C}'_C(\gamma,\rho) + \mathcal{E}'_C(\gamma,\rho)|$. Putting the total sum $P_C + P_e = 1$, i.e. $P_C + P_e$ is 100%, the weights are defined simply by

$$W_C = \frac{P_C}{P_C + P_e}, \quad W_e = \frac{P_e}{P_C + P_e}, \tag{3.159}$$

The weight for the best fit of R.
At the values $\lambda = 1/37$ (i.e. $r_c = 0.0115$), $\gamma = 1.1706$, and $\rho = 1.6320$, for which we have minimal $E_{mol} = -1.144$ and optimal $R = 1.40$, we get the numerical values of the weights,

$$W_e = 0.84\% \tag{3.160}$$

for the pure isoelectronium phase, and $W_C = 100\% - W_e = 99.16\%$ for the Coloumb phase.

The weight for the best fit of E_{mol}.
At the values $\lambda = 1/5$ (i.e. $r_c = 0.0833$ a.u.), $\gamma = 1.2005$, and $\rho = 1.5827$, for which we have minimal $E_{mol} = -1.173$ a.u. and optimal $R = 1.318$ a.u., we obtain

$$W_e = 6.16\%, \quad W_C = 93.84\%. \tag{3.161}$$

From the above two cases, one can see that the weight of pure isoelectronium phase is estimated to be

$$W_e \simeq 1...6\%, \tag{3.162}$$

for the predicted variational energy $E_{mol} = -1.143... - 1.173$ a.u.

The biggest possible weight.
Note that in our V_e-based model the biggest allowed value of λ is $\lambda = 1/4$

(i.e. $r_c = 0.1034$) because $\lambda < 1/3$, to avoid divergency of the Coloumb integral $\mathcal{C}_e$. For this value of λ, we obtain minimal $E_{mol} = -1.182$ a.u. and optimal $R = 1.297$ a.u. This value corresponds to the *biggest* possible weight of the pure isoelectronium phase,

$$W_e = 7.32\%, \tag{3.163}$$

within our approximate model.

The following three remarks are in order.

(i) We consider the existence of this upper limit, $W_e \leq 7.32\%$, as a highly remarkable implication of our V_e-model noting however that it may be artifact of the use of the exponential screened Coloumb potential.

(ii) Another remarkable implication is due to the condition, $\lambda^{-1} =$ *integer number*, obtained for the case of Hulten potential. One can see from Table 2 that the energy E_{mol} varies *discretely* with the discrete variation of λ^{-1}. This means that there is no possibility to make a "smooth fit". For example, at $\lambda = 1/5$, we have $E_{mol} = -1.173$, and the *nearest* two values, $\lambda = 1/4$ and $\lambda = 1/6$, give us $E_{mol} = -1.182$ and $E_{mol} = -1.167$, respectively. Therefore, owing to the above condition the model becomes *more predicitive*.

(iii) Numerical calculation shows that the formal use of the exact Coloumb integral $\mathcal{C}'_g$, given by Eq.(3.128), of the *Gaussian* screened Coloumb potential, instead of $\mathcal{C}'_e$, in Eq.(3.147) gives us approximately the same fits. Namely, the best fit of the energy is achieved at $\lambda = 1/5$, with $r_c = 0.1042$, optimal $R = 1.323$, and minimal $E_{mol} = -1.172$. Also, the best fit of $R = 1.40$ is at $\lambda = 1/29$, for which $r_c = 0.0147$ and minimal $E_{mol} = -1.144$. Here, we have used the same exchange integral as it is for the case of exponential screened potential so these fits have been presented just for a comparison with our basic fits, and to check the results. Note that for the case of Gaussian screened Coloumb integral we have no restriction on the allowed values of λ. Analysis shows that, at big values of λ, e.g. at $\lambda > 4$, the integral $\mathcal{C}'_g$, given by (3.128), rapidly oscillates in the region of small ρ ($\rho < 0.5$). This means that when the correlation length r_c becomes comparable to the internuclear distance an effect of instability of the molecule arises. This can be viewed as a natural criterium to fix the upper limit of λ. Normally, we use the values $\lambda < 1$, for which case there are no any oscillations of $\mathcal{C}'_g$ (see Fig. 9).

λ^{-1}	r_c, a.u.	R_{opt}, a.u.	E_{min}, a.u.
4	0.10337035071618050	1.297162129235449	-1.181516949656805
5	0.08329699109108888	1.318393698326879	-1.172984902150024
6	0.06975270534273319	1.333205576478603	-1.167271240301846
7	0.05999677404817234	1.344092354783681	-1.163188554065554
8	0.05263465942162049	1.352417789644028	-1.160130284706318
9	0.04688158804756491	1.358984317233049	-1.157755960428922
10	0.04226204990365446	1.364292909163710	-1.155860292450436
11	0.03847110142927672	1.368671725082009	-1.154312372623724
12	0.03530417706681329	1.372344384866235	-1.153024886026671
13	0.03261892720535206	1.375468373051375	-1.151937408039373
14	0.03031323689615631	1.378157728092548	-1.151006817317425
15	0.02831194904031777	1.380497017045902	-1.150201529091051
16	0.02655851947236431	1.382550255552670	-1.149497886394651
17	0.02500959113834722	1.384366780045693	-1.148877823925501
18	0.02363136168905809	1.385985219224291	-1.148327310762828
19	0.02239708901865092	1.387436244558651	-1.147835285349041
20	0.02128533948435381	1.388744515712491	-1.147392910500336
21	0.02027873303335994	1.389930082626193	-1.146993041730378
22	0.01936302821907175	1.391009413196452	-1.146629840949675
23	0.01852644434336641	1.391996158084790	-1.146298491232105
24	0.01775915199935013	1.392901727808297	-1.145994983116511
25	0.01705288514774330	1.393735733699196	-1.145715952370148
26	0.01640064219648127	1.394506328745493	-1.145458555325045
27	0.01579645313764336	1.395220473843219	-1.145220372020229
28	0.01523519631632570	1.395884147817973	-1.144999330178493
29	0.01471245291356761	1.396502514589167	-1.144793644973560
30	0.01422439038752817	1.397080057337240	-1.144601770891686

Table 2: The total minimal energy E_{min} and the optimal internuclear distance R_{opt} as functions of the correlation length r_c. The exponential screened Coloumb potential V_e case (see Figures 15 and 16).

λ^{-1}	r_c, a.u.	R_{opt}, a.u.	E_{min}, a.u.
31	0.01376766836566138	1.397620687025853	-1.144422362947838
32	0.01333936209977966	1.398127830817745	-1.144254245203342
33	0.01293689977547854	1.398604504597664	-1.144096385030938
34	0.01255801083612469	1.399053372836414	-1.143947871939897
35	0.01220068312791624	1.399476798299823	-1.143807900045981
36	0.01186312715793131	1.399876883556063	-1.143675753475045
37	0.01154374612489787	1.400255505817128	-1.143550794143290
39	0.01095393745919852	1.400954915288619	-1.143320213707519
40	0.01068107105944273	1.401278573036792	-1.143213620508321
41	0.01042146833640030	1.401586548200467	-1.143112256673494
42	0.01017418516195214	1.401879953246168	-1.143015746732479
43	0.00993836493541500	1.402159797887369	-1.142923750307661
44	0.00971322867044429	1.402427000676349	-1.142835958109381
45	0.00949806639934841	1.402682399061957	-1.142752088467028
46	0.00929222969498477	1.402926758144872	-1.142671884314343
47	0.00909512514431396	1.403160778323019	-1.142595110561057
48	0.00890620863525624	1.403385101987775	-1.142521551794315
49	0.00872498034101540	1.403600319405678	-1.142451010262626
50	0.00855098030451296	1.403806973898863	-1.142383304102633
51	0.00838378454080327	1.404005566419838	-1.142318265775268
52	0.00822300158793934	1.404196559601683	-1.142255740683024
53	0.00806826944722482	1.404380381352424	-1.142195585944305
54	0.00791925286251402	1.404557428052374	-1.142137669304475
55	0.00777564089552400	1.404728067404676	-1.142081868166104
56	0.00763714476025456	1.404892640982100	-1.142028068723488
57	0.00750349588477794	1.405051466507240	-1.141976165188595
58	0.00737444417302681	1.405204839898059	-1.141926059097351
59	0.00724975644291090	1.405353037106507	-1.141877658686723
60	0.00712921502024112	1.405496315774223	-1.141830878334298

Table 3: The total minimal energy E_{min} and the optimal internuclear distance R_{opt} as functions of the correlation length r_c. The exponential screened Coloumb potential V_e case (see Figures 15 and 16).

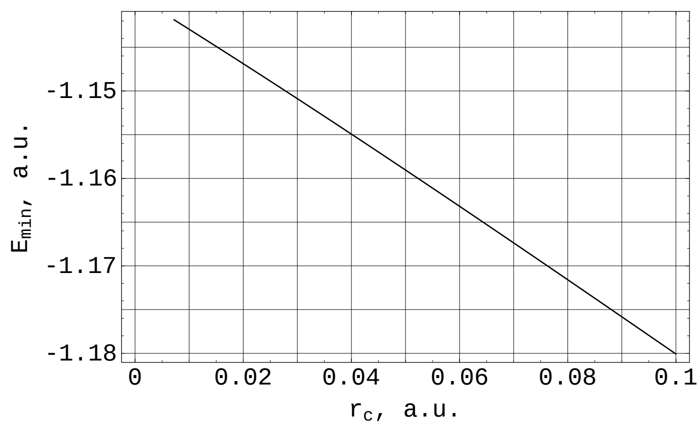

Figure 15: The total minimal energy E_{min} as a function of the correlation length r_c. The exponential screened Coloumb potential V_e case (see Tables 2 and 3).

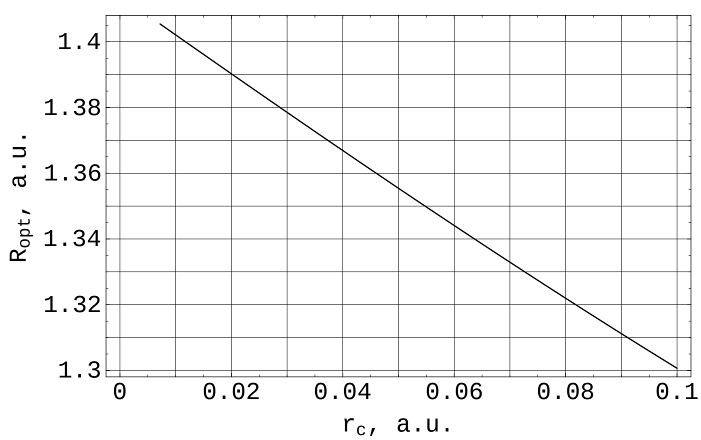

Figure 16: The optimal internuclear distance R_{opt} as a function of the correlation length r_c. The exponential screened Coloumb potential V_e case (see Tables 2 and 3).

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